# Supporting Information

# Toward Perfect Regiocontrol for $\beta$-Selective Cyclopolymerization Using a Ru-Based Olefin Metathesis Catalyst

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# 1. General experimental

Materials

All reagents which are commercially available from Sigma-Aldrich®, Tokyo Chemical Industry Co. Ltd., Acros Organics, Alfa Aesar®, without additional notes, were used without further purification. **Ru2** was provided from Materia Inc. (C633, CAS# 1352916-84-7), and is also commercially available from Sigma-Aldrich®. Dichloromethane for the polymerization were purified by Glass Contour Organic Solvent Purification System, and degassed further by Ar bubbling for 10 minutes before performing reactions. Thin-layer chromatography (TLC) was carried out on MERCK TLC silica gel 60 F254 and flash column chromatography was performed using MERCK silica gel 60 (0.040~0.063 mm).

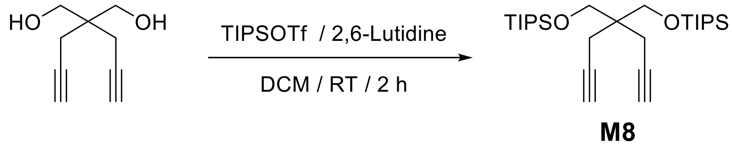
Characterization

$^{1}$H-NMR and $^{13}$C-NMR were recorded by Varian/Oxford As-500 (500 MHz for $^{1}$H and 125 MHz for $^{13}$C) and Agilent 400-MR (400 MHz for $^{1}$H and 100 MHz for $^{13}$C) spectrometers. $^{13}$C NMR for the polymers were mainly recorded by Bruker (600 MHz for $^{1}$H and 150 MHz for $^{13}$C) spectrometers in the National Instrumentation Center for Environmental Management (NICEM) at SNU. High resolution mass spectroscopy (HRMS) analyses were performed by the ultrahigh resolution ESI Q-TOF mass spectrometer (Bruker, Germany) in the Sogang Centre for Research Facilities. Size exclusion chromatography (SEC) analyses were carried out with Waters system (1515 pump, 2414 refractive index detector) and Shodex GPC LF-804 column eluted with THF (GPC grade, Honeywell Burdick & Jackson®) and filtered with a 0.2 μm PTFE filter (Whatman®). Flow rate was 1.0 mL/min and temperature of column was maintained at 35 °C. UV-Vis spectra were obtained by Jasco Inc. UV/vis Spectrometer V-650. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were carried out under $N_2$ gas at a scan rate of 10 °C/min with Q50 and Q10 model devices, respectively, from TA Instruments. Cyclic voltammetry (CV) measurements were carried out on a CHI 660 Electrochemical Analyzer (CH Instruments, Insc., Texas, USA).

## 2. Experimental procedures for the preparation of the monomers

**Ru1**,[1] **Ru3**,[2] **M1-M4**,[3] **M5**,[4] **M6**,[5] **M7**,[4] **M9**,[4] **M10**,[6] and **M11**,[3] **7** were prepared by literature methods.

**M8** (3,3,9,9-tetraisopropyl-2,10-dimethyl-6,6-di(prop-2-yn-1-yl)-4,8-dioxa-3,9-disilaundecane)



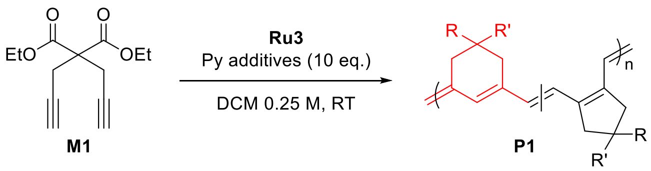

To a solution of 4,4-Bis(hydroxymethyl)-1,6-heptadiyne[7] (460 mg, 3.0 mmol) in dichloromethane (9 mL), 2,6-lutidine (1.4 mL, 12 mmol) was added and the mixture was cooled down to 0 °C, followed by the addition of triisopropylsilyl trifluoromethanesulfonate (1.1 mL, 6 mmol). After stirring overnight at room temperature, the mixture was quenched by aqueous $NH_4Cl$ solution. Product was extracted with ethyl acetate and organic layer was washed with brine. The organic layer was dried with $MgSO_4$ and concentrated to give a yellow colored solid. It was purified by flash column chromatography on silica gel (Hexane 100%) to afford compound **M8** as a colorless liquid (1.2 g, 84%). $^1H$ NMR (500 MHz, $CDCl_3$): δ 3.71 (s, 4H), 2.37 (d, J = 2.7 Hz, 4H), 1.95 (t, J = 2.6 Hz, 2H), 1.07 (s, 42H).; $^{13}C$ NMR (125 MHz, $CDCl_3$): δ 81.6, 70.5, 64.1, 44.2, 21.4, 18.2, 12.2.; HR-MS (ESI) m/z for $C_{27}H_{52}NaO_2Si_2$ [**M**+Na]$^+$, calcd. 487.3398, found: 487.3399.

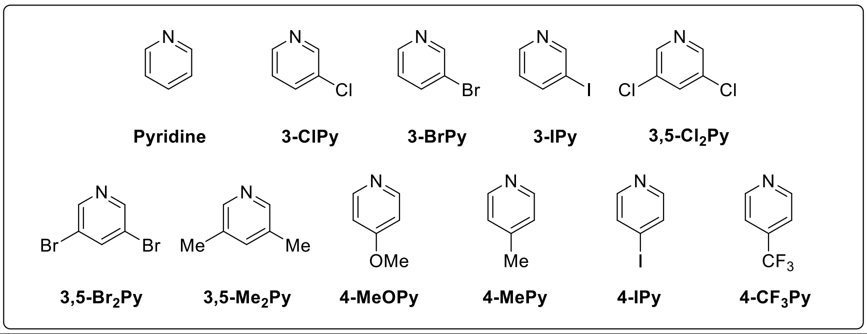
## 3. General procedure for the cyclopolymerization

A 5-mL sized screw-cap vial with septum was flame dried and charged with monomer and a magnetic bar. The vial was purged with argon four times, and degassed anhydrous dichloromethane was added. After the Ar-purged catalyst (**Ru1**-**Ru3**) in another 5-mL vial was dissolved in dichloromethane, the solution was rapidly injected to the monomer solution at experimental temperature (RT) under vigorous stirring. The reaction was quenched by excess ethyl vinyl ether after desired reaction time, and partially precipitated in hexane at -78 °C, remaining small amount of crude mixture (~10%). Obtained solid was filtered and dried in vacuo. Monomer conversion was calculated from the $^{1}$H NMR spectrum of the remaining crude mixture.

## 4. Polymerization results in Table 1

<**Table S1**. Cyclopolymerization of **M1** using **Ru3** with various pyridine additives>




| | additive | M/I/Add | conv[a] | yield[b] | $M_n$ (Da)[c] | PDI[c] | 6:5 ($^{1}$H)[a] |
|---|---|---|---|---|---|---|---|
| **1** | none | 30/1/- | 76% | 58% | 6.8k | 1.58 | 5.9:1 |
| **2** | Pyridine | 30/1/10 | 83% | 46% | 6.6k | 1.48 | 6.1:1 |
| **3** | 3-ClPy | 30/1/10 | 85% | 76% | 7.1k | 1.63 | 8.8:1 |
| **4** | 3-BrPy | 30/1/10 | 45% | 37% | 6.0k | 1.43 | 12.5:1 |
| **5** | 3-IPy | 30/1/10 | 73% | 15% | 5.3k | 1.43 | 13.8:1 |
| **6** | 3,5-Cl$_2$Py | 30/1/10 | 91% | 65% | 8.1k | 1.62 | 11.6:1 |
| **7** | 3,5-Br$_2$Py | 30/1/10 | 6.1% | - | - | - | |
| **8** | 3,5-Me$_2$Py | 30/1/10 | 29% | 29% | 6.4k | 1.46 | 4.3:1 |
| **9** | 4-MeOPy | 30/1/10 | 18% | 11% | 3.5k | 1.31 | 1.9:1 |
| **10** | 4-MePy | 30/1/10 | 4.5% | - | - | - | - |
| **11** | 4-IPy | 30/1/10 | 74% | 22% | 5.4k | 1.48 | 14.3:1 |
| **12** | 4-CF$_3$Py | 30/1/10 | 6.2% | - | - | - | |

[a]Determined from $^{1}$H NMR. [b]Precipitated in Hex at -78℃.
[c]Determined by THF SEC calibrated using polystyrene standards.

## 5. $^{1}H$ and $^{13}C$ NMR characterization of polymers

Poly(**M1**)
$^{1}H$ (500 MHz, $CDCl_3$): δ 7.04 – 5.73 (br m, 2H), 4.40 – 3.88 (br s, 4H), 3.62 – 2.69 (br m, 4H), 1.50 – 1.01 (br s, 6H).; $^{13}C$ (125 MHz, $CDCl_3$): δ 171.9, 170.0, 134.5, 134.1, 133.1, 131.8, 61.7, 58.1, 54.7, 35.1, 32.4, 14.2.

Poly(**M2**)
$^{1}H$ (500 MHz, $CDCl_3$): δ 6.94 – 5.69 (br m, 2H), 5.22 – 4.82 (br s, 2H), 3.62 – 2.60 (br m, 4H), 1.50 – 0.97 (br s, 12H); $^{13}C$ (125 MHz, $CDCl_3$): δ 171.4, 170.3, 136.5, 134.4, 134.1, 133.1, 131.9, 69.0, 57.9, 54.5, 35.0, 32.2, 21.6.

Poly(**M3**)
$^{1}H$ (500 MHz, $CDCl_3$): δ 6.93 – 5.71 (br m, 2H), 3.56 – 2.46 (br m, 4H), 1.74 – 1.07 (br m, 18H); $^{13}C$ (125 MHz, $CDCl_3$): δ 171.1, 170.1, 134.6, 134.3, 133.3, 131.9, 81.4, 59.1, 55.7, 35.3, 32.4, 27.7.

Poly(**M4**)
$^{1}H$ (500 MHz, $CDCl_3$): δ 6.85 – 5.63 (br m, 2H), 3.71 – 2.52 (br m, 12H), 1.30 – 0.66 (br s, 12H); $^{13}C$ (125 MHz, $CDCl_3$): δ 171.8, 170.7, 135.1, 134.1, 130.9, 130.2, 57.3, 53.2, 41.5, 40.6, 37.8, 33.5, 13.9, 12.8.

Poly(**M5**)
$^{1}H$ (500 MHz, $CDCl_3$): δ 6.98 – 5.57 (br m, 2H), 4.44 – 3.45 (br m, 4H), 2.98 – 1.91 (br m, 4H), 1.57 – 0.66 (br m, 18H); $^{13}C$ (125 MHz, $CDCl_3$): δ 178.0, 177.9, 133.9, 132.8, 67.2, 66.3, 39.1, 37.9, 34.3, 31.6, 27.3.

Poly(**M6**)
$^{1}H$ NMR (500 MHz, $CDCl_3$): δ 7.06 – 5.47 (br m, 2H), 4.01 – 3.21 (br s, 2H), 3.21 – 1.47 (br m, 4H), 1.12 – 0.57 (br s, 9H), 0.37 – -0.40 (br s, 6H); $^{13}C$ NMR (125 MHz, $CDCl_3$): δ 137.0, 134.6, 130.9, 67.3, 37.2, 32.6, 29.8, 26.1, 18.5, -5.2.

Poly(**M7**)
$^{1}H$ NMR (500 MHz, $CDCl_3$): δ 6.96 – 5.58 (br m, 2H), 3.79 – 3.07 (br s, 4H), 2.71 – 1.92 (br d, 4H), 1.07 – 0.63 (br s, 18H), 0.24 – -0.26 (br m, 12H); $^{13}C$ NMR (125 MHz, $CDCl_3$): δ 135.6, 135.4, 133.8, 132.4, 65.3, 40.6, 33.5, 30.6, 26.2, 18.4, -5.3.

Poly(**M8**)
$^{1}H$ NMR (500 MHz, $CDCl_3$): δ 6.91 – 5.56 (br m, 2H), 3.89 – 3.18 (br s, 4H), 2.78 – 2.09 (br d, 4H), 1.38 – 0.71 (br s, 42H); $^{13}C$ NMR (125 MHz, $CDCl_3$): δ 135.9, 135.2, 133.3, 132.3, 66.4, 66.0, 41.3, 33.6, 31.0, 18.3, 12.2.

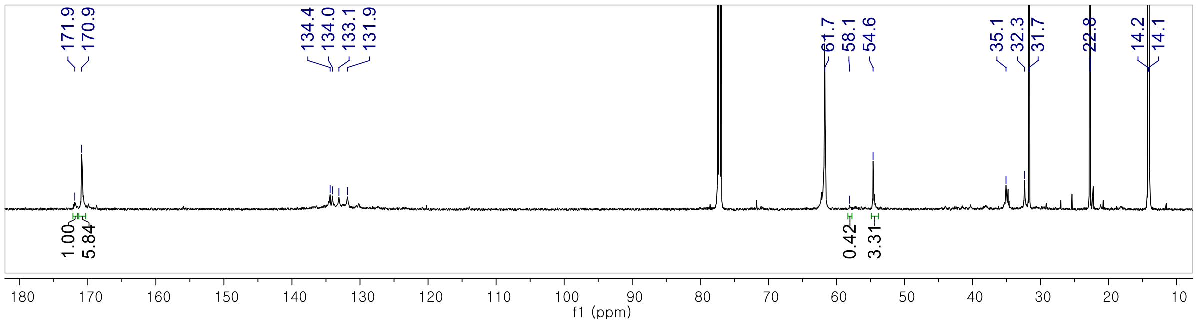
Poly(**M9**)
$^{1}H$ NMR (500 MHz, $CDCl_3$): δ 7.46 – 6.99 (br m, 10H), 4.63 – 4.19 (br s, 4H), 3.61 – 3.10 (br s, 4H), 2.86 – 2.21 (br m, 4H); $^{13}C$ NMR (125 MHz, $CDCl_3$): δ 139.2, 135.6, 135.1, 133.4, 132.3, 128.3, 127.3, 73.3, 73.3, 39.6, 34.4, 31.4.

Poly(**M10**)
$^{1}H$ NMR (500 MHz, $CDCl_3$): δ 6.92 – 5.62 (br m, 2H), 3.40 (br d, 8H), 2.80 – 2.07 (br m, 4H), 1.39 – 0.92 (br s, 6H); $^{13}C$ NMR (125 MHz, $CDCl_3$): δ 135.9, 135.4, 133.0, 132.0, 74.2, 73.7, 73.6, 67.0, 66.8, 39.4, 34.1, 31.2, 15.3.

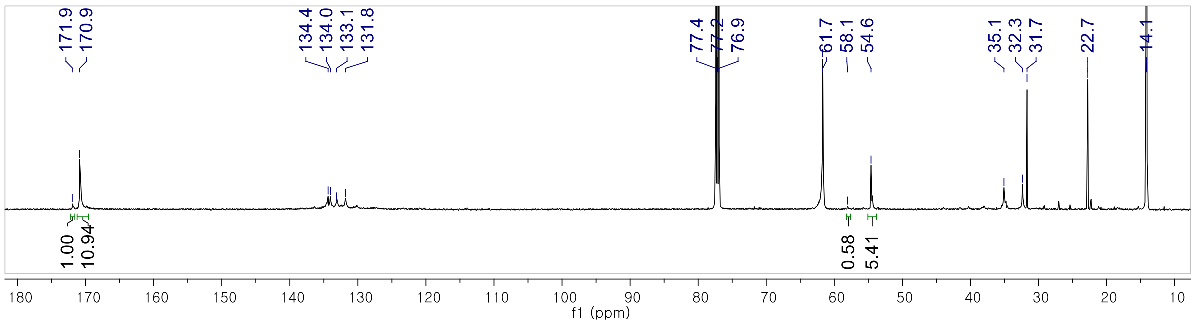
Poly(**M11**)
$^{1}H$ NMR (500 MHz, $CDCl_3$): δ 7.00 – 5.58 (br m, 2H), 4.35 – 3.79 (br s, 2H), 3.79 – 2.14 (br m, 4H), 1.65 – 0.82 (br d, 9H), 0.56 – -0.22 (br s, 9H); $^{13}C$ NMR (125 MHz, $CDCl_3$): δ 174.2, 137.5, 136.5, 134.2, 131.7, 130.3, 76.4, 60.4, 56.8, 56.6, 56.3, 56.2, 35.9, 33.7, 32.7, 30.2, 26.8, 14.2, 2.7.

## 6. $^{13}$C NMR spectra of the polymers in Table 1

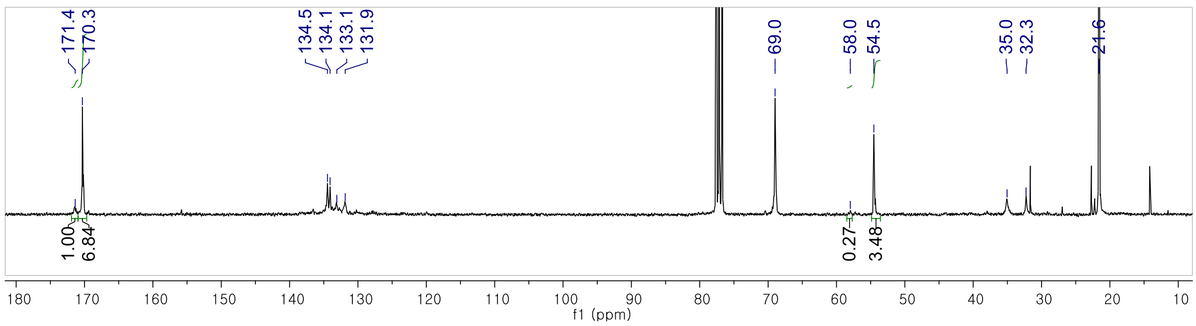
Those spectra were used for the determination of the ratio between five- and six-ring on the polymer backbone.



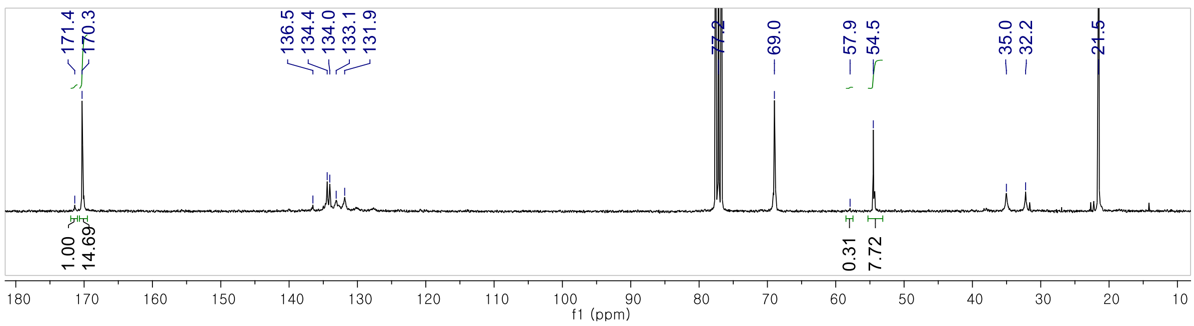

<**Figure S1.** $^{13}$C NMR spectra of polymer from **entry 1** in **Table 1**>



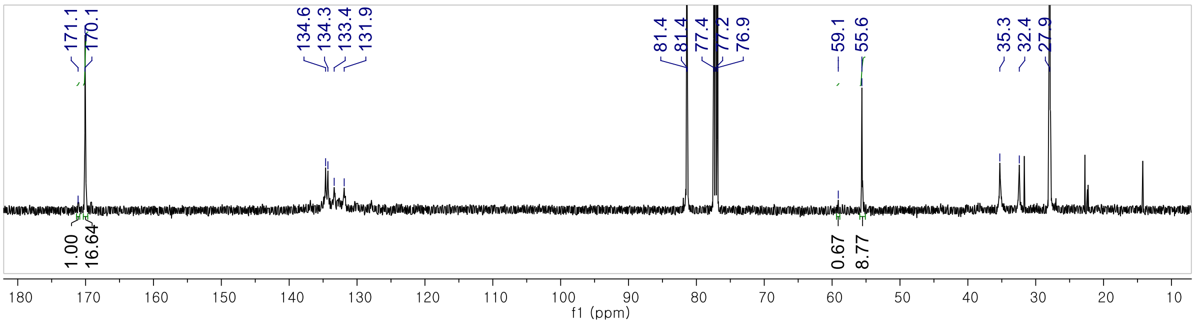

<**Figure S2.** $^{13}$C NMR spectra of polymer from **entry 2** in **Table 1**>



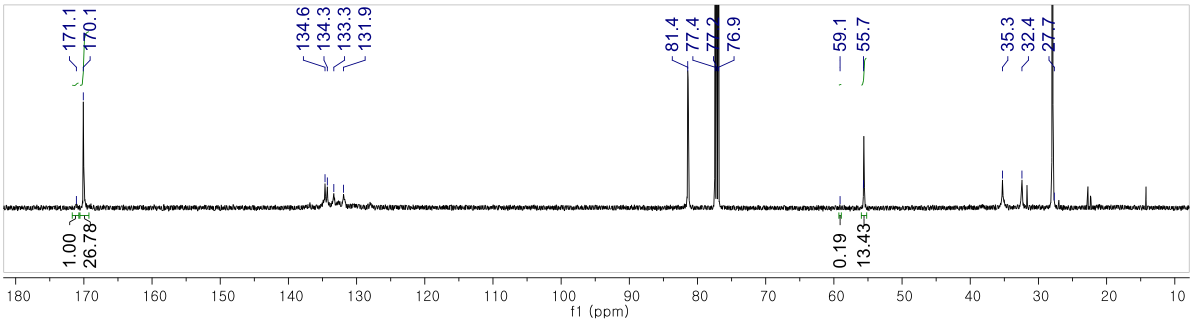

<**Figure S3.** $^{13}$C NMR spectra of polymer from **entry 3** in **Table 1**>



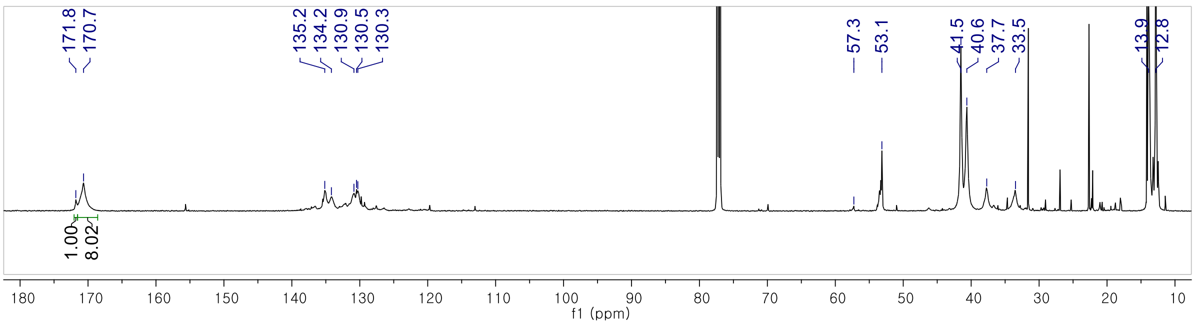

<**Figure S4.** $^{13}$C NMR spectra of polymer from **entry 4** in **Table 1**>



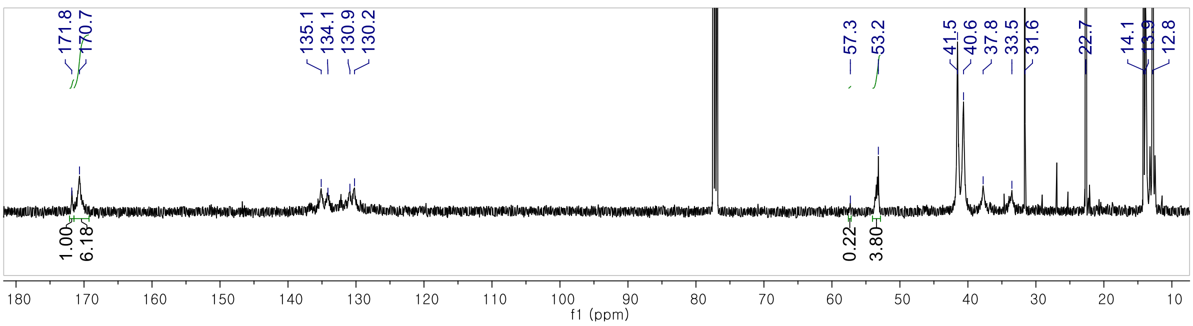

<**Figure S5.** $^{13}$C NMR spectra of polymer from **entry 5** in **Table 1**>



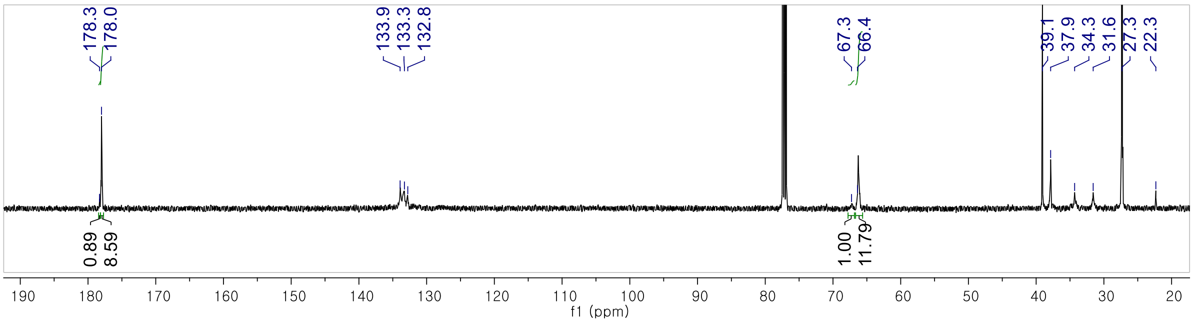

<**Figure S6.** $^{13}$C NMR spectra of polymer from **entry 6** in **Table 1**>



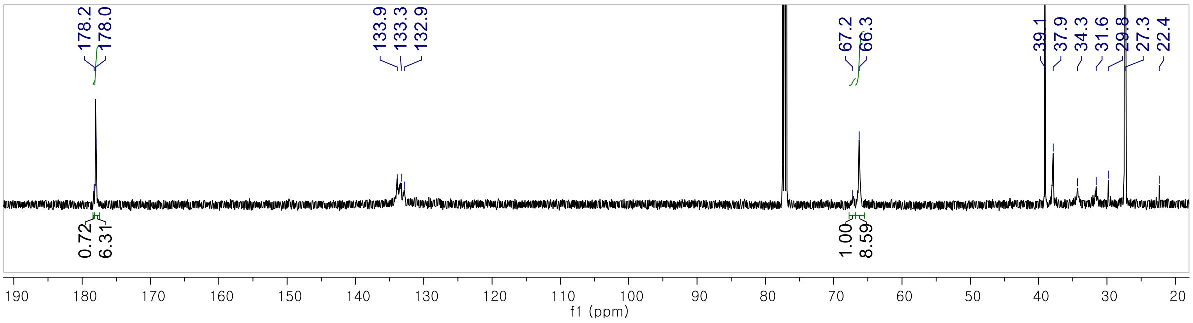

<**Figure S7.** $^{13}$C NMR spectra of polymer from **entry 7** in **Table 1**>



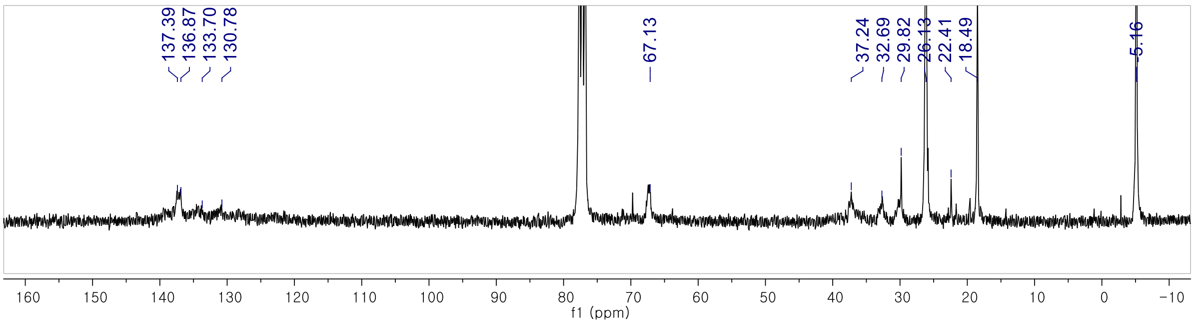

<**Figure S8.** $^{13}$C NMR spectra of polymer from **entry 8** in **Table 1**>



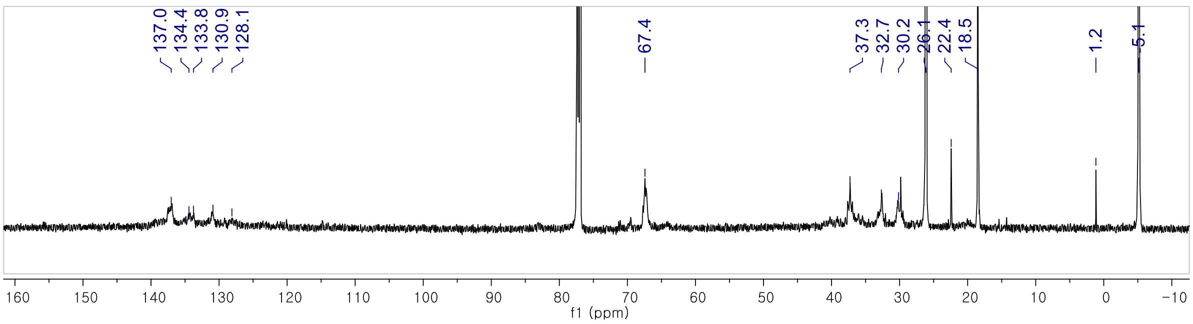

<**Figure S9.** $^{13}C$ NMR spectra of polymer from **entry 9** in **Table 1**>



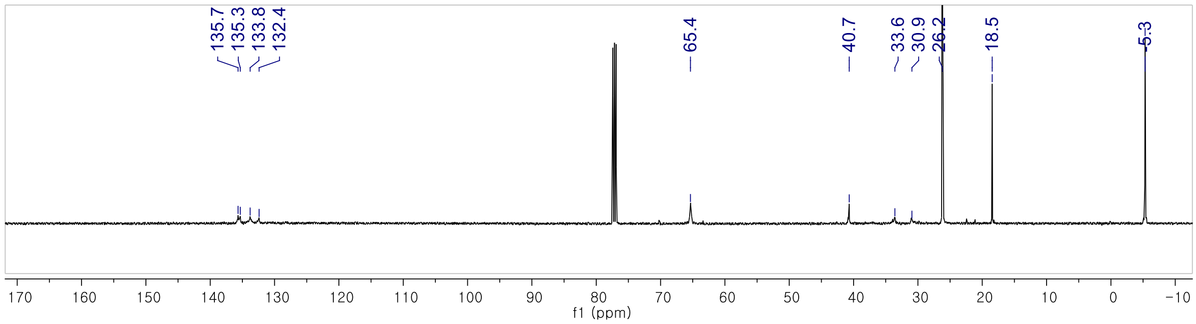

<**Figure S10.** $^{13}C$ NMR spectra of polymer from **entry 10** in **Table 1**>



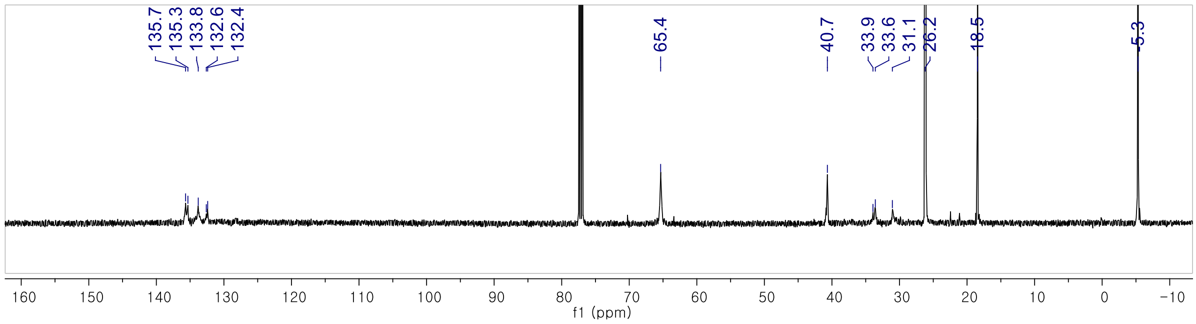

<**Figure S11.** $^{13}C$ NMR spectra of polymer from **entry 11** in **Table 1**>



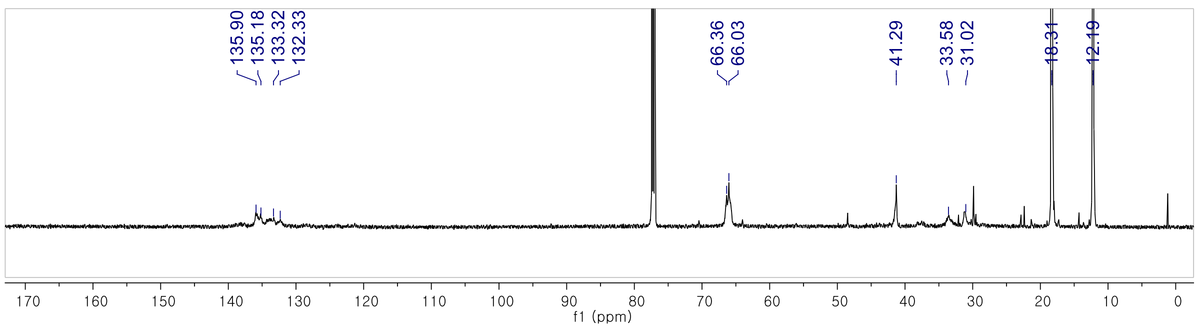

<**Figure S12.** $^{13}C$ NMR spectra of polymer from **entry 12** in **Table 1**>



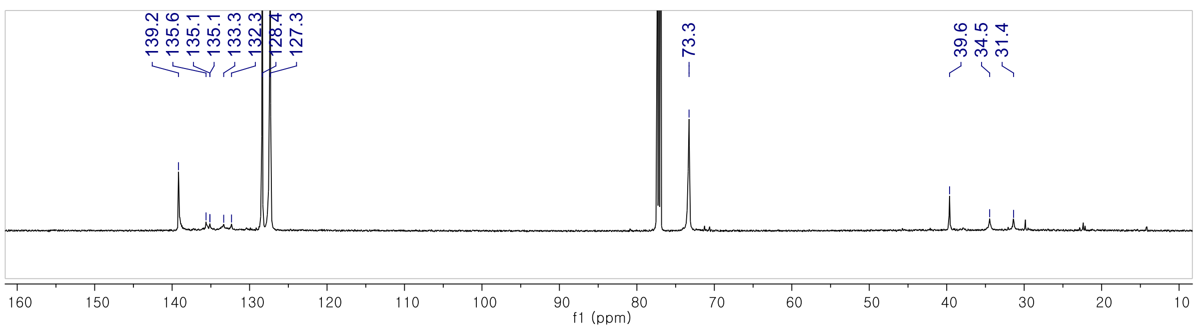

<**Figure S13.** $^{13}$C NMR spectra of polymer from **entry 13** in **Table 1**>



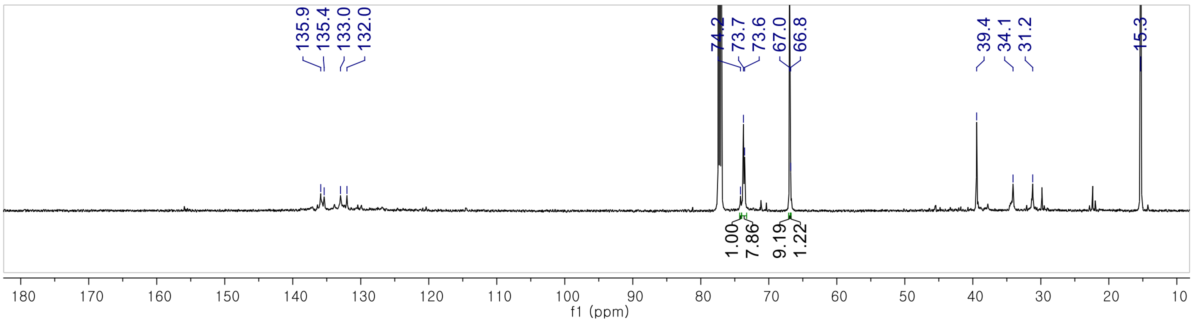

<**Figure S14.** $^{13}$C NMR spectra of polymer from **entry 14** in **Table 1**>



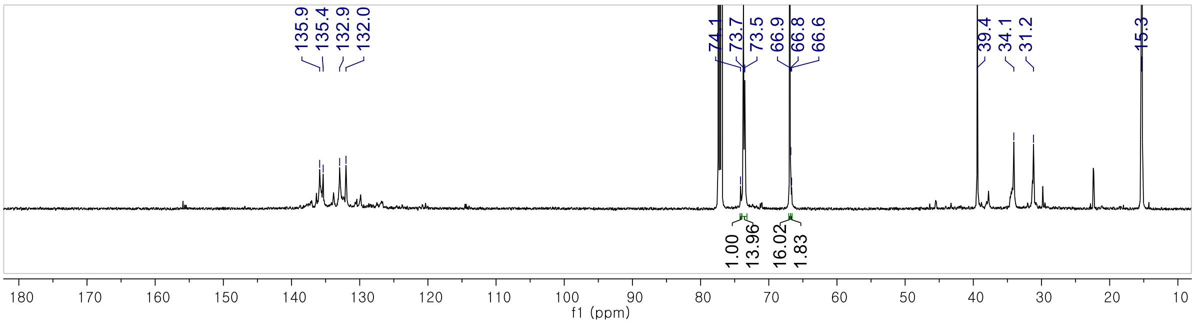

<**Figure S15.** $^{13}$C NMR spectra of polymer from **entry 16** in **Table 1**>



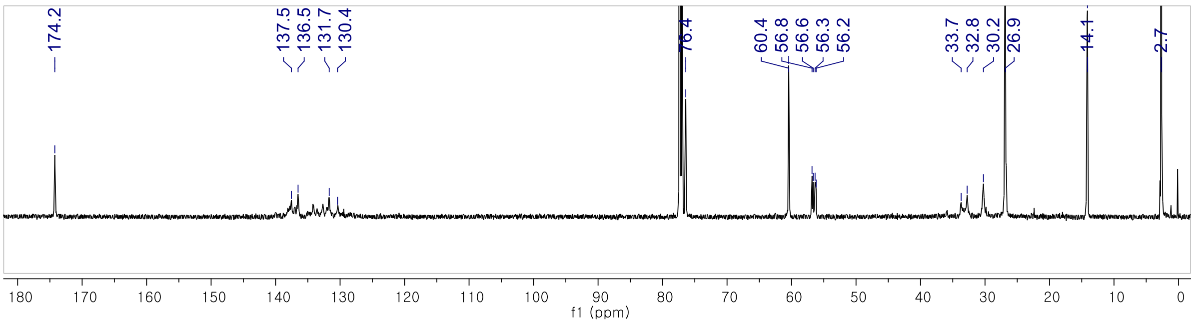

<**Figure S16.** $^{13}$C NMR spectra of polymer from **entry 18** in **Table 1**>



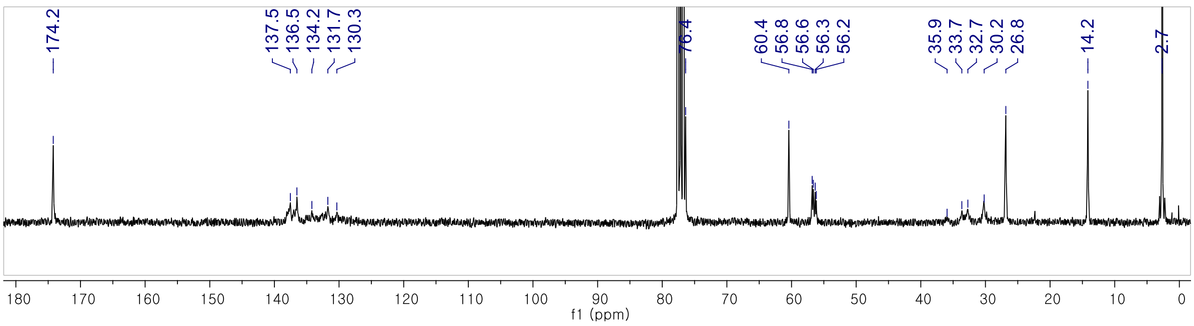

<**Figure S17.** $^{13}$C NMR spectra of polymer from **entry 19** in **Table 1**>




<**Figure S18.** $^{13}$C NMR spectra of polymer from **entry 20** in **Table 1**>



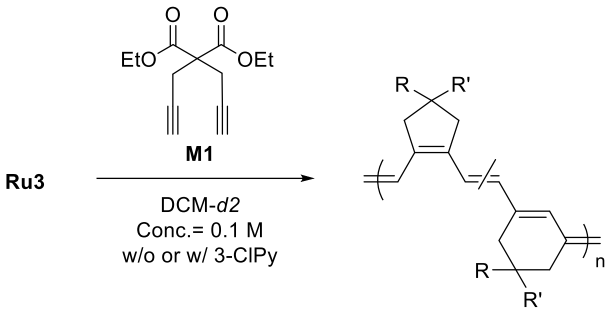

<**Figure S19.** $^{13}$C NMR spectra of polymer from **entry 21** in **Table 1**>



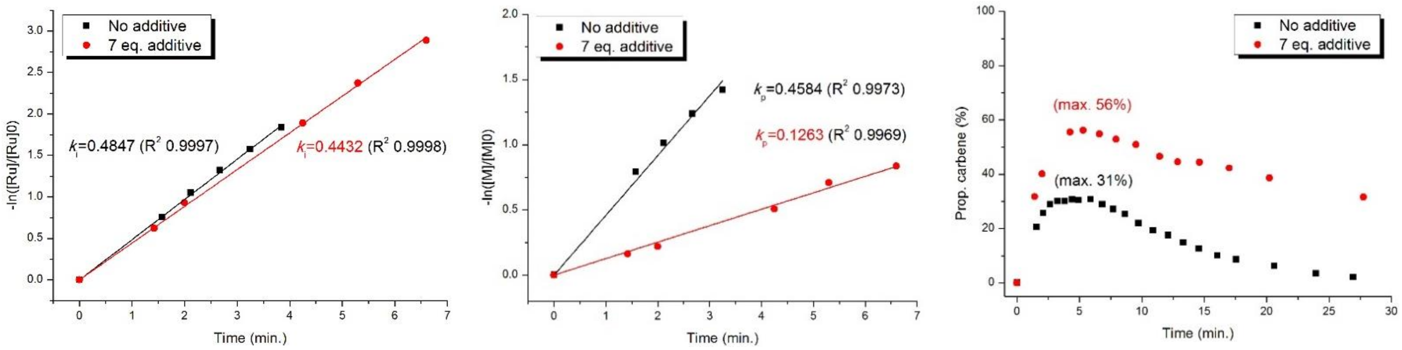

<**Figure S20.** $^{13}$C NMR spectra of polymer from **entry 22** in **Table 1**>

## 7. *In situ* NMR experiment: procedure and data

**Ru3** (0.003 mmol, 1 eq) and hexamethyldisilane (internal standard, 5 μl) were dissolved in DCM-*d2* (400 μL). Initial benzylidene was measured by integral ratio of **Ru3** to hexamethyldisilane in $^{1}$H NMR spectrum. (After the addition of 7 eq of the pyridine additive,) Monomer (0.06 mmol, 20 eq) solution in DCM-*d2* (200 μl) was added to the **Ru3** solution and mixed by shaking NMR tube for 5 sec. The reaction was monitored by $^{1}$H NMR over time. The $k_i$ or $k_p$ values were obtained from the slope of linear – ln [**Ru3**]/[**Ru3**]$_0$ or – ln [M]/[M]$_0$ vs. time graphs, respectively.

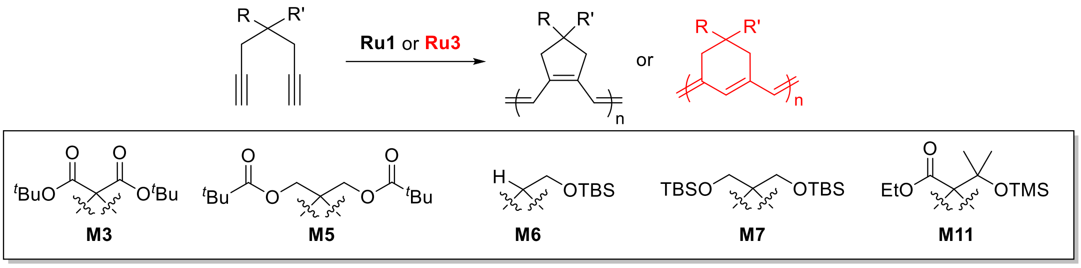



| M/I/Add | $k_i$ | $k_p$ | $k_i/k_p$ |
|---|---|---|---|
| 20/1/- | 0.4847 | 0.4584 | 1.0574 |
| 20/1/7 | 0.4432 | 0.1263 | 3.5091 |



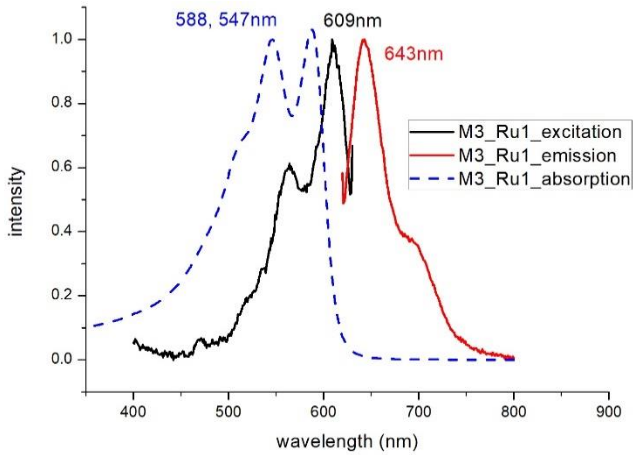
## 8. Physical and thermal properties of the polymers

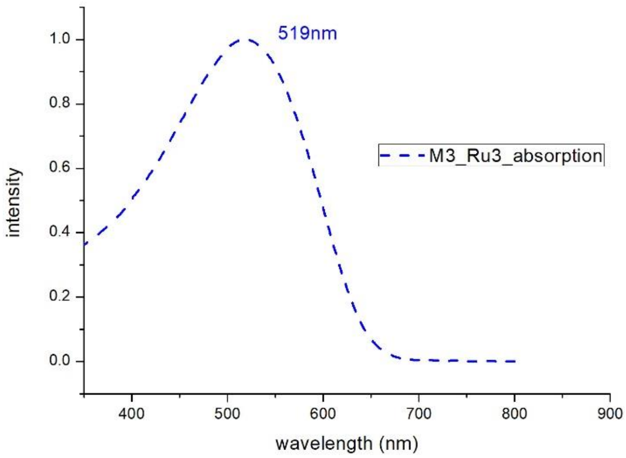
<**Table S2**. Comparison of the properties (five- vs. six-membered rings)>

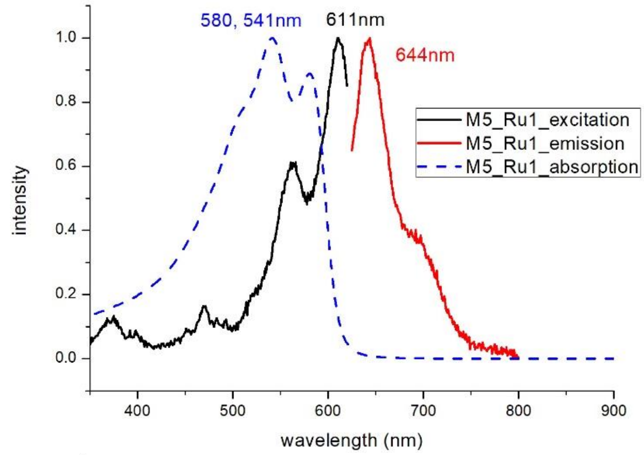


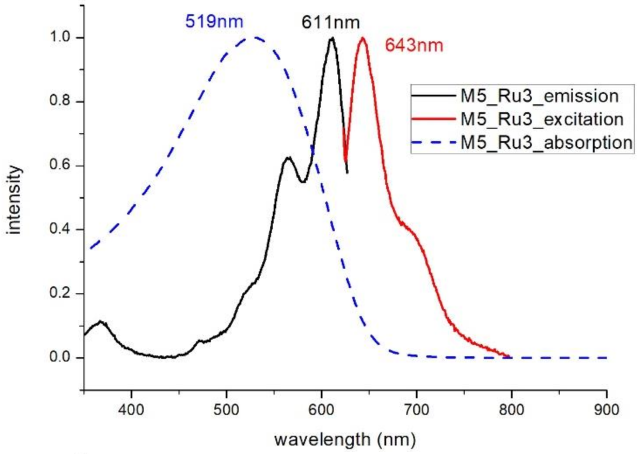

| Monomer | Cat | Solution | | Film | | $E_{HOMO}$ (eV) | PL (nm) | Stokes shift (nm) | $T_d$ (℃) | $T_g$ (℃) |
|---|---|---|---|---|---|---|---|---|---|---|
| | | $\lambda_{max}$ (nm) | $E_g$ (eV) | $\lambda_{max}$ (nm) | $E_g$ (eV) | | | | | |
| **M3** | **Ru1** | 588, 547 | 2.02 | 515 | 2.01 | -4.98 | 643 | 96 | 242 | 107 |
| | **Ru3** | 519 | 1.92 | 477 | 1.93 | -4.73 | nd | nd | 219 | 127 |
| **M5** | **Ru1** | 580, 541 | 2.03 | 576, 535 | 2.01 | -4.98 | 640 | 99 | 360 | 133 |
| | **Ru3** | 527 | 1.91 | 494 | 1.91 | -4.83 | 643 | 116 | 326 | 106 |
| **M6** | **Ru1** | 586, 546 | 2.00 | 548 | 1.94 | -4.77 | 645 | 99 | 320 | nd |
| | **Ru3** | 508 | 1.94 | 503 | 1.87 | -4.62 | 644 | 124 | 313 | 71 |
| **M7** | **Ru1** | 594, 552 | 1.97 | 572, 529 | 2.02 | -5.12 | 641 | 89 | 357 | 92 |
| | **Ru3** | 539 | 1.85 | 517 | 1.86 | -5.12 | nd | nd | 370 | 93 |
| **M11** | **Ru1** | 598, 556 | 1.97 | 598, 551 | 1.94 | -4.74 | 643 | 87 | 334 | 83 |
| | **Ru3** | 537 | 1.83 | 496 | 1.86 | -4.52 | 641 | 104 | 361 | 100 |

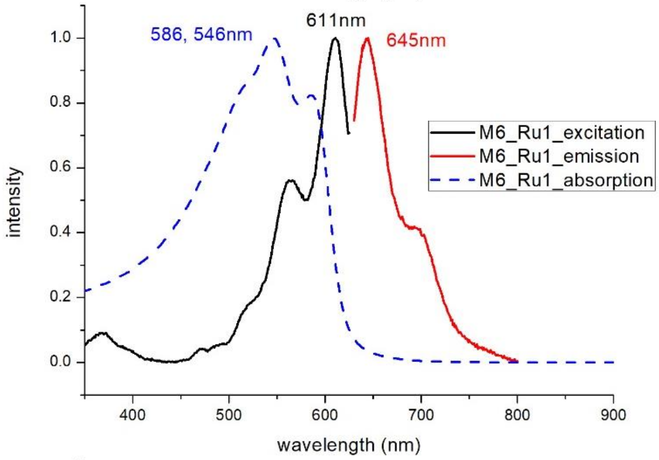
## 9. UV-Vis and PL spectra of the polymers

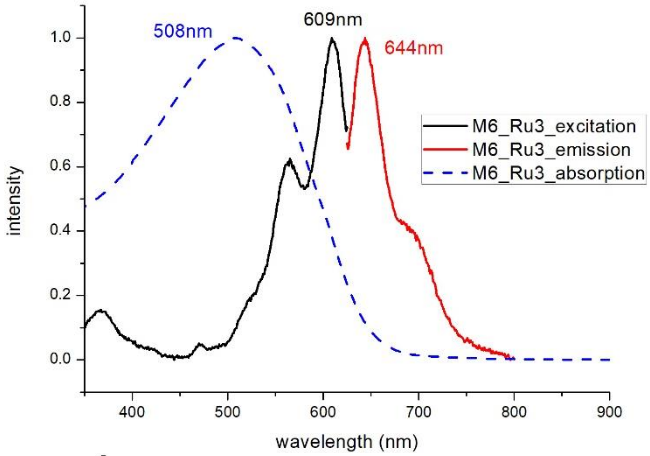


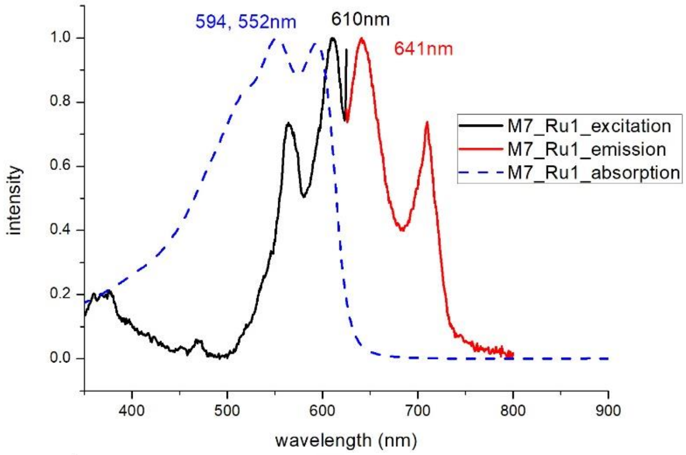



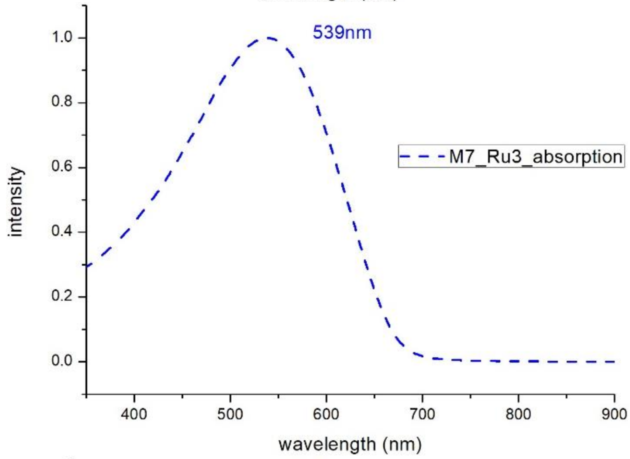

580, 541nm
611nm
644nm
M5_Ru1_excitation
M5_Ru1_emission
M5_Ru1_absorption
intensity
wavelength (nm)

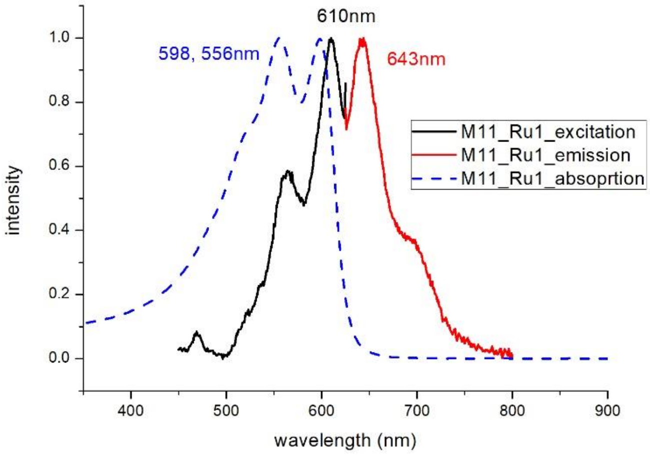

519nm
611nm
643nm
M5_Ru3_emission
M5_Ru3_excitation
M5_Ru3_absorption
intensity
wavelength (nm)

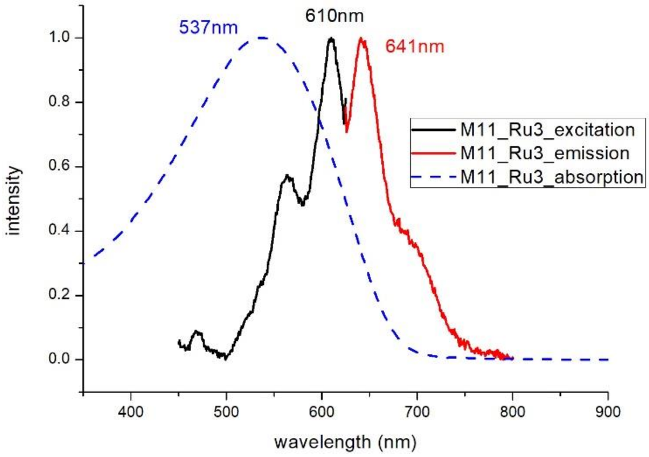

586, 546nm
611nm
645nm
M6_Ru1_excitation
M6_Ru1_emission
M6_Ru1_absorption
intensity
wavelength (nm)


508nm
609nm
644nm
M6_Ru3_excitation
M6_Ru3_emission
M6_Ru3_absorption
intensity
wavelength (nm)


594, 552nm
610nm
641nm
M7_Ru1_excitation
M7_Ru1_emission
M7_Ru1_absorption
intensity
wavelength (nm)

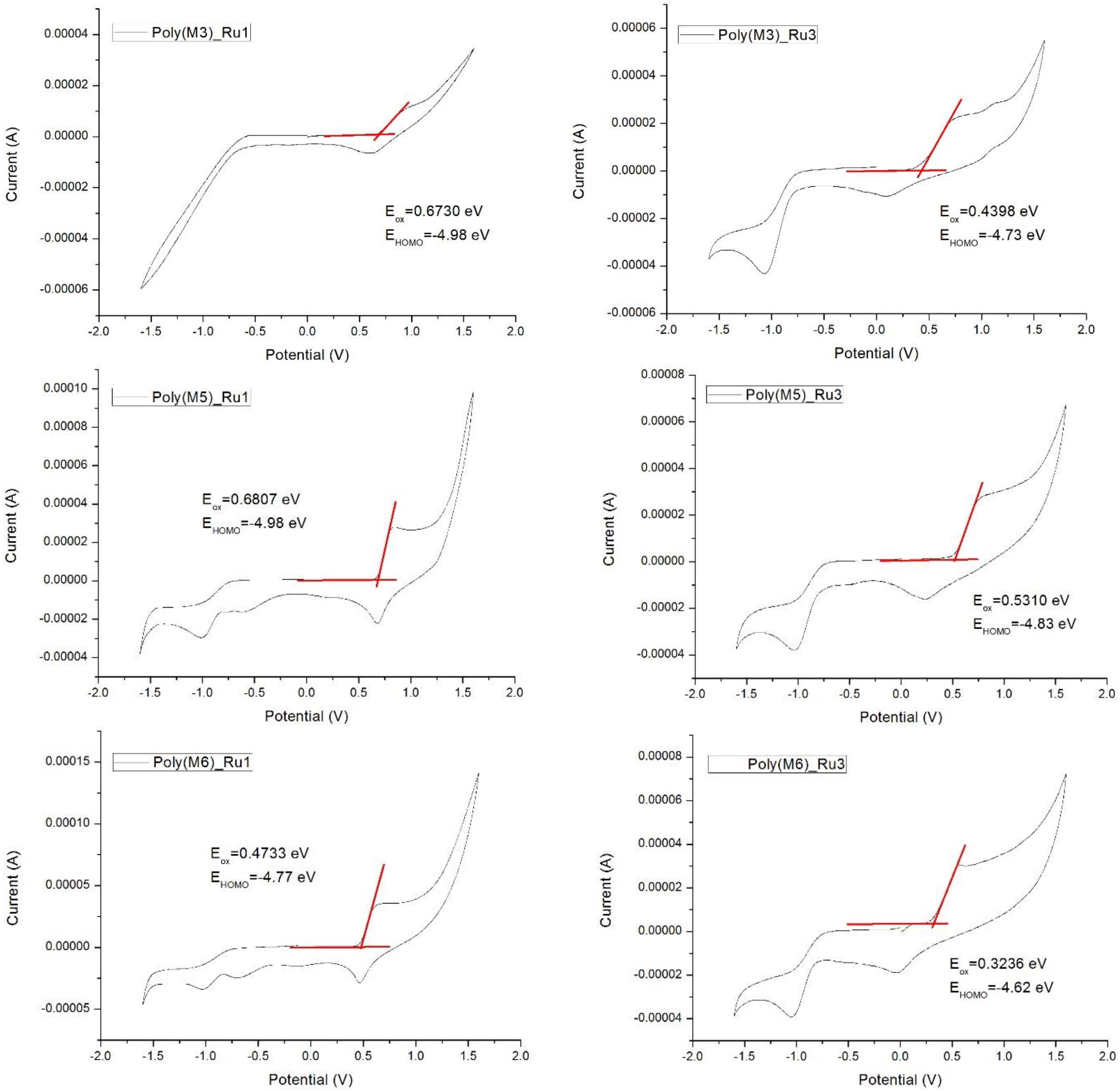

539nm
M7_Ru3_absorption
intensity
wavelength (nm)

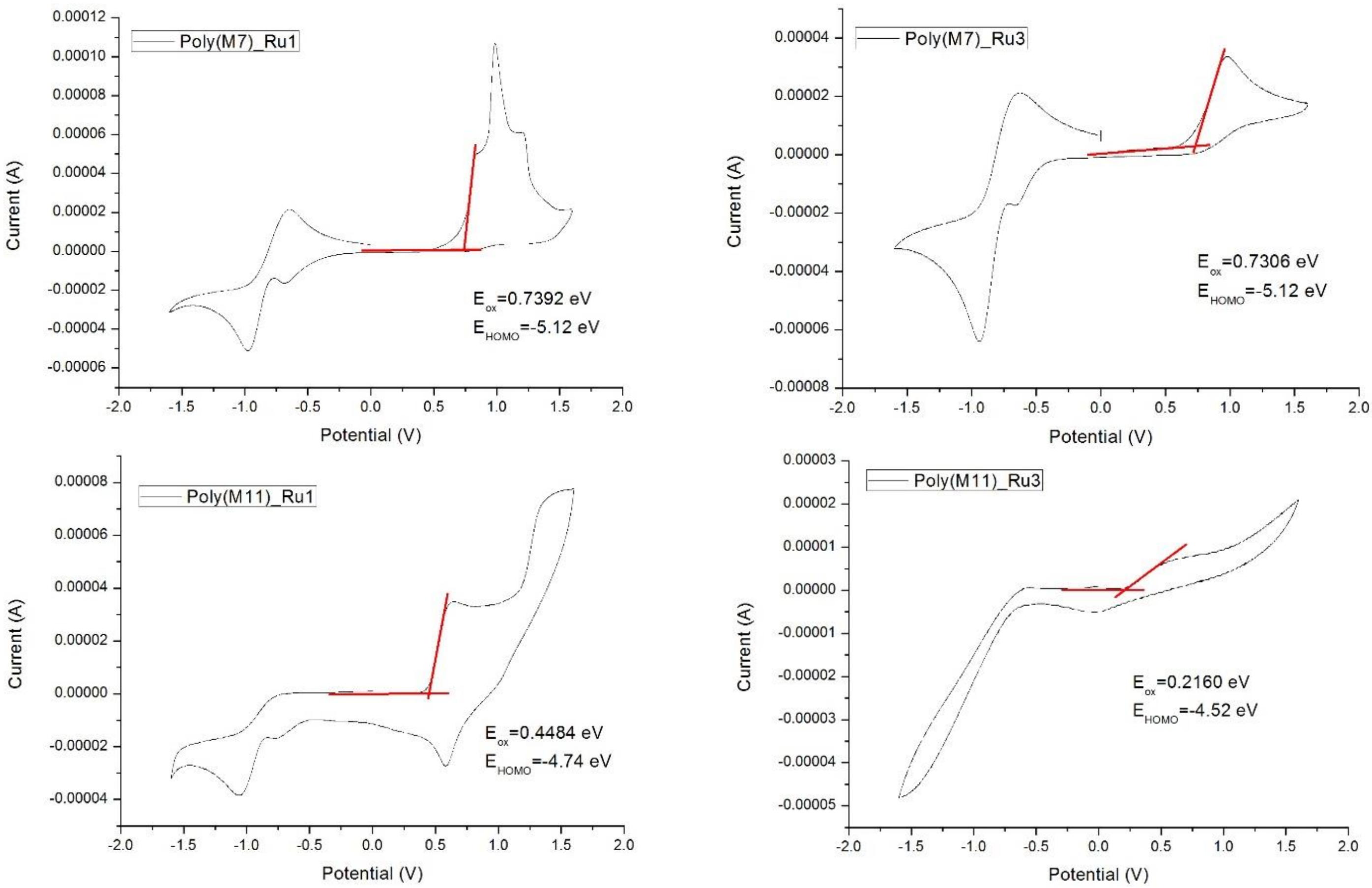

598, 556nm
610nm
643nm
M11_Ru1_excitation
M11_Ru1_emission
M11_Ru1_absoprtion
intensity
wavelength (nm)


537nm
610nm
641nm
M11_Ru3_excitation
M11_Ru3_emission
M11_Ru3_absorption
intensity
wavelength (nm)

## 10. Cyclic voltammograms of the polymers

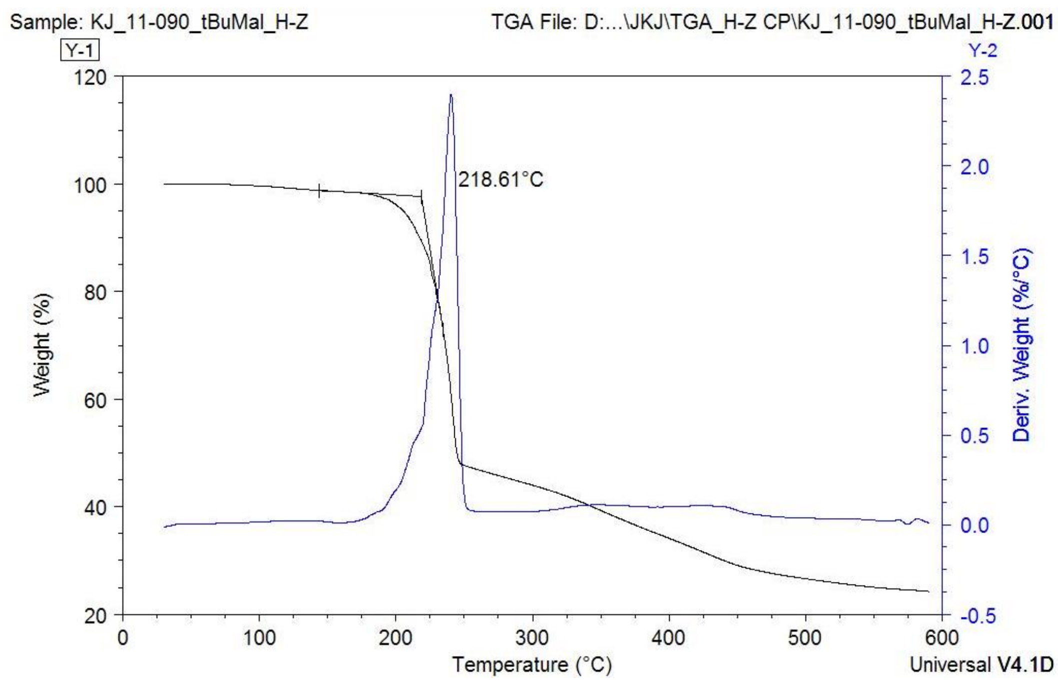
Cyclic voltammetry (CV) measurement was carried out at the room temperature on a CHI 660 Electrochemical Analyzer (CH Instruments, Insc., Texas, USA) using a degassed acetonitrile solution of tetrabutylammonium hexafluorophosphate ($Bu_4NPF_6$, 0.1 M). Polymer solution was prepared by dissolving the polymer in dichloromethane (10 mg/ml). Cyclic voltammogram was recorded using the glassy carbon working electrode and a reference electrode of $Ag/Ag^+$ (0.1 M $AgNO_3$ in acetonitrile) with a platinum wire counter electrode at a scan rate of 50 mV/s. The absolute energy level was obtained using ferrocene/ferrocenium as an internal standard. The oxidation potential of ferrocene was regarded as - 4.8 eV.



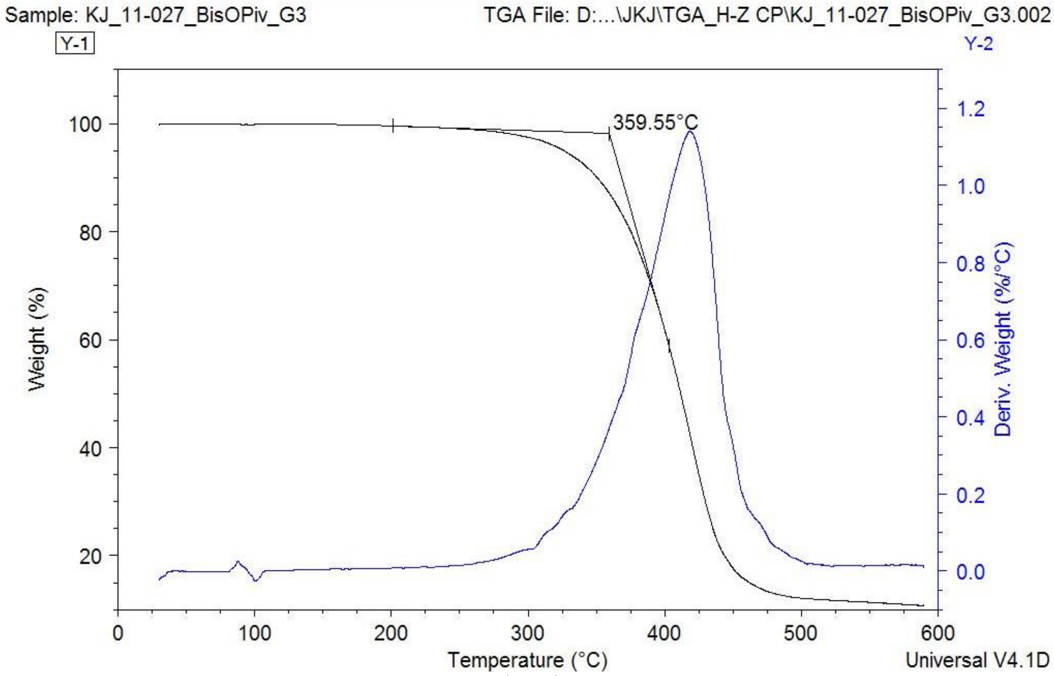



## 11. TGA and DSC curves of the polymers

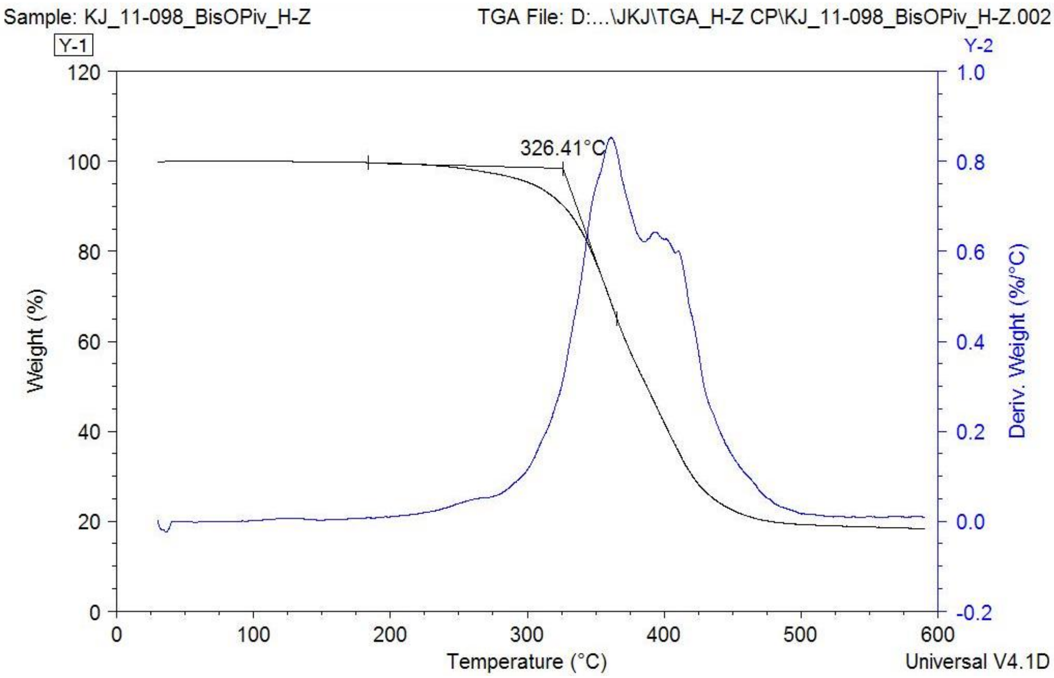
TGA and DSC data for Poly(**M3**) synthesized using **Ru1** catalyst were reported previously.[3]



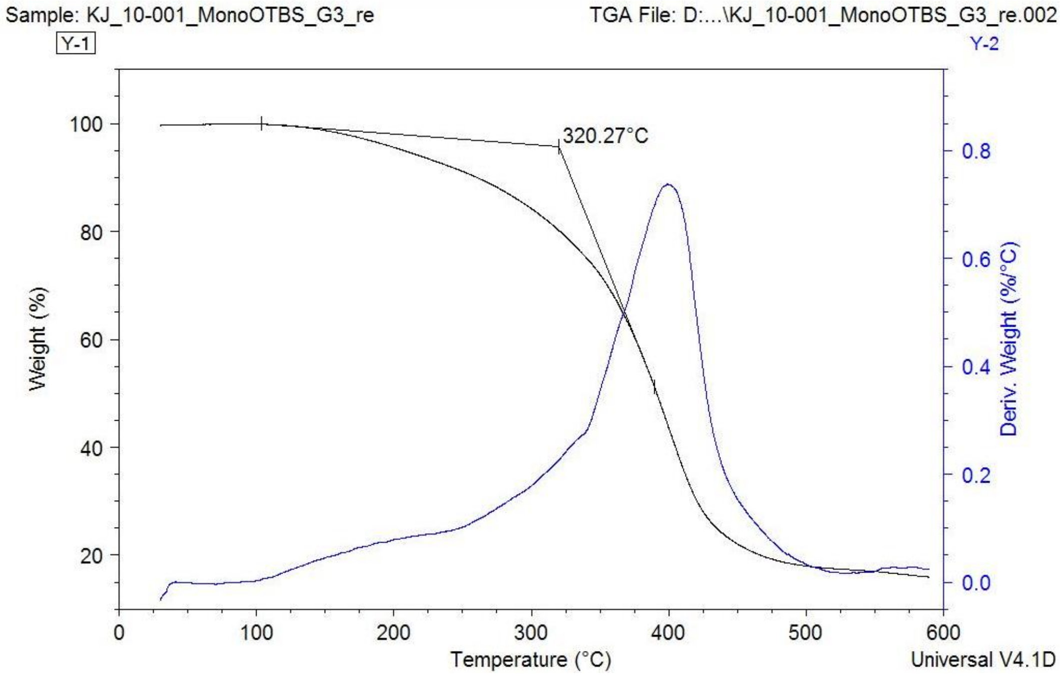

<**Figure S21.** TGA curves of Poly(**M3**) synthesized using **Ru3** catalyst>



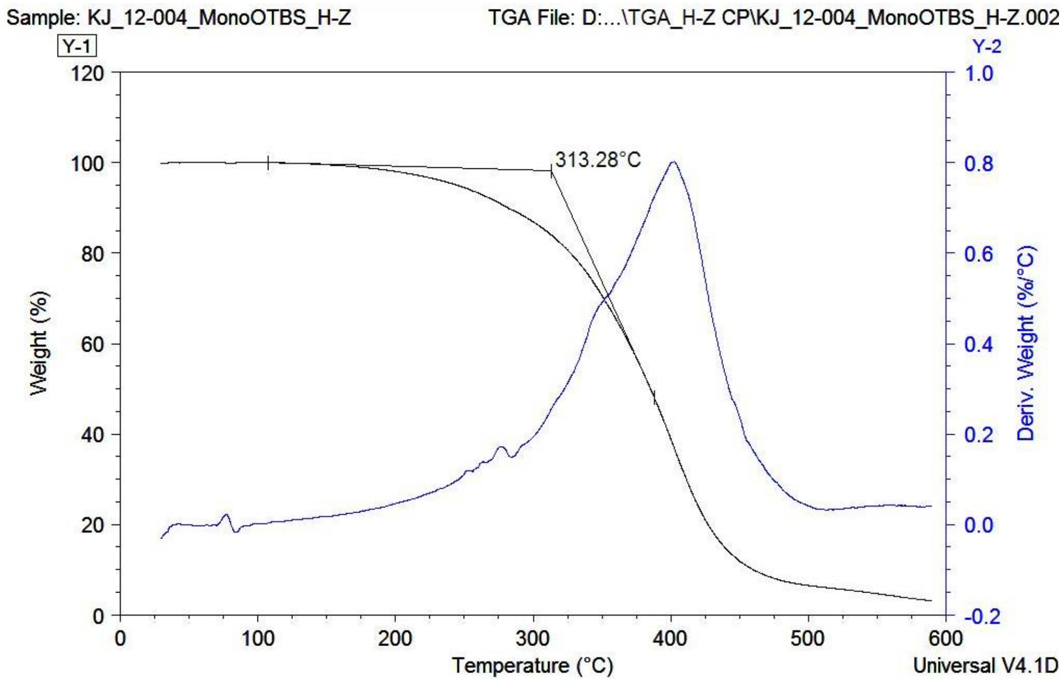

<**Figure S22.** TGA curves of Poly(**M5**) synthesized using **Ru1** catalyst>



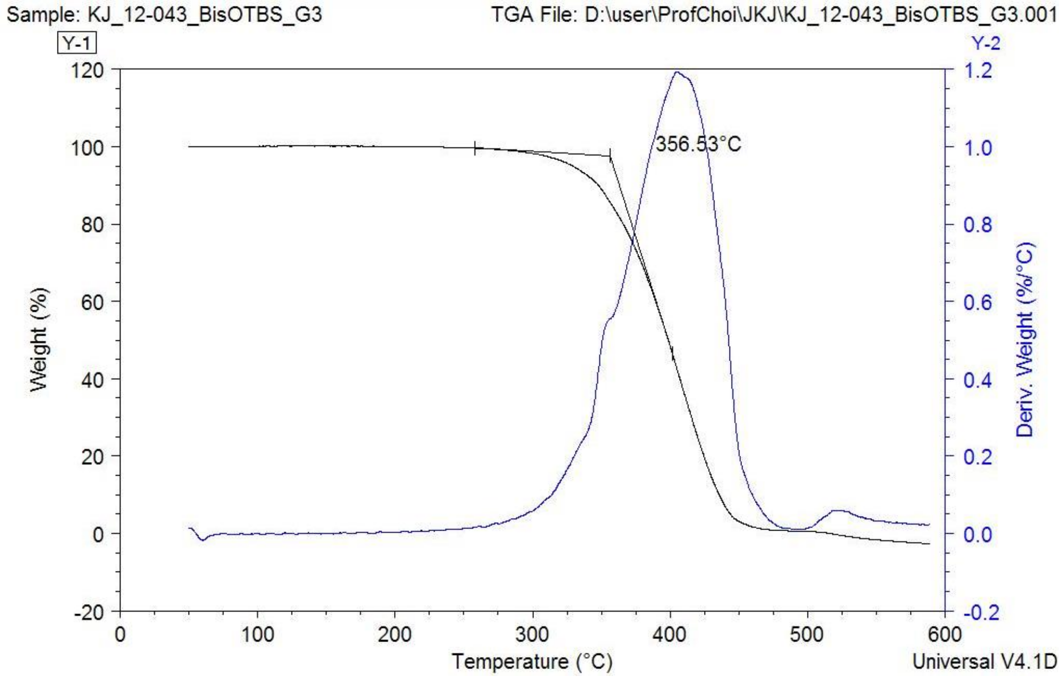

<**Figure S23.** TGA curves of Poly(**M5**) synthesized using **Ru3** catalyst>



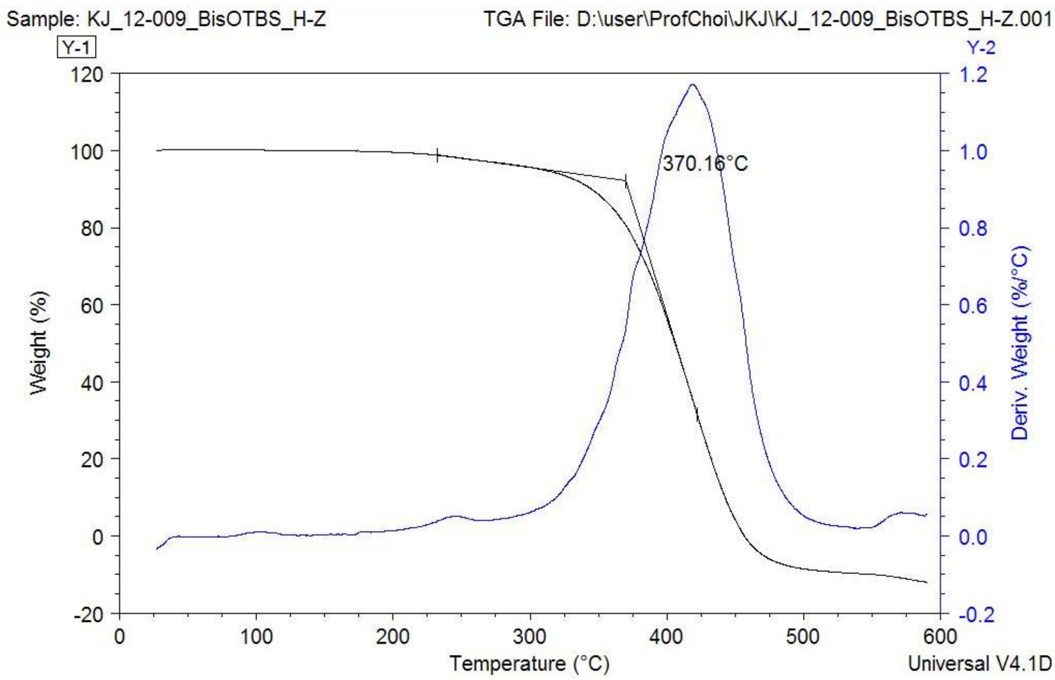

<**Figure S24.** TGA curves of Poly(**M6**) synthesized using **Ru1** catalyst>



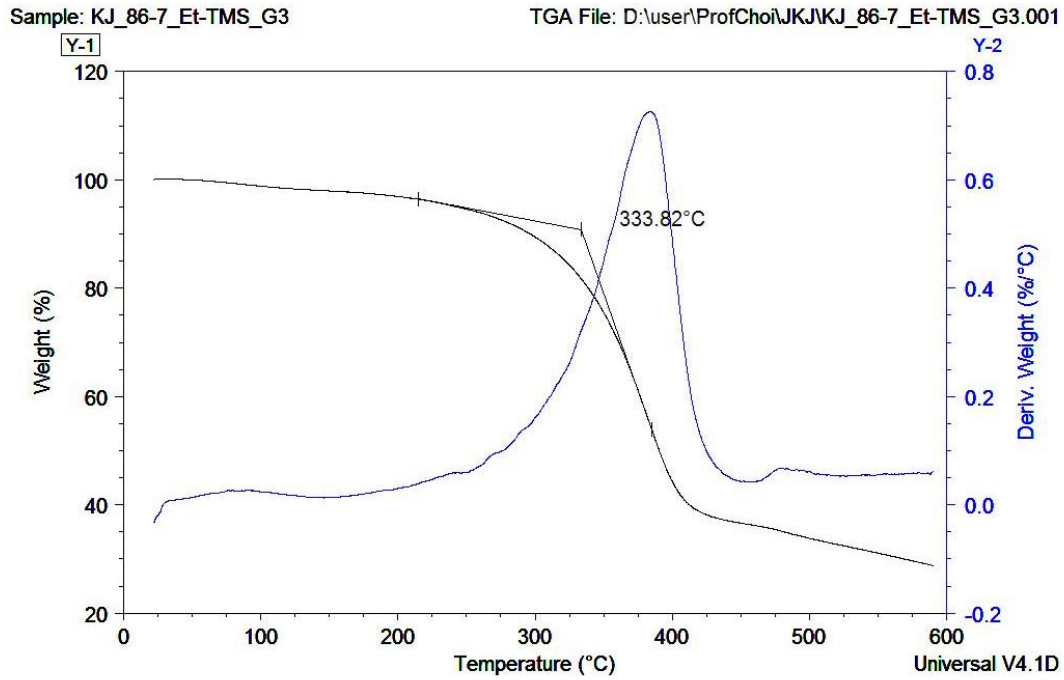

<**Figure S25.** TGA curves of Poly(**M6**) synthesized using **Ru3** catalyst>



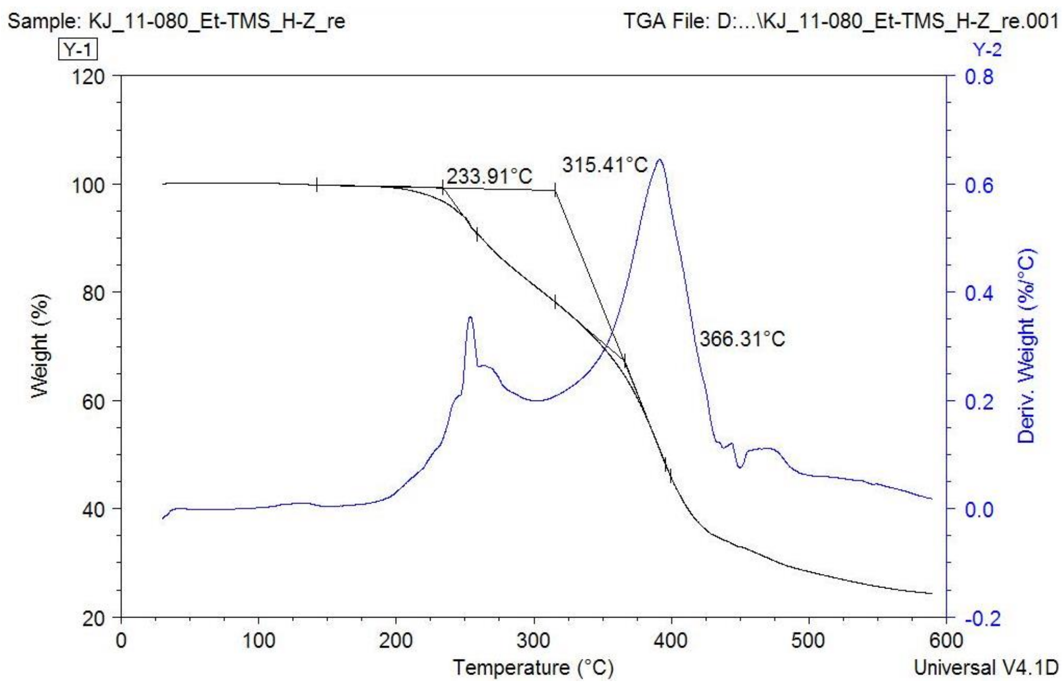

<**Figure S26.** TGA curves of Poly(**M7**) synthesized using **Ru1** catalyst>



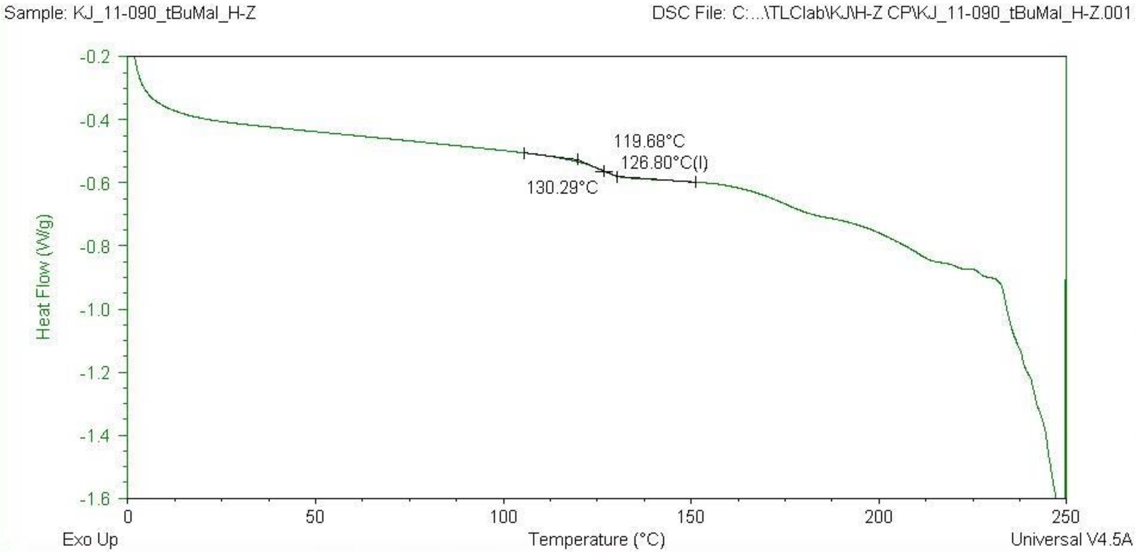

<**Figure S27.** TGA curves of Poly(**M7**) synthesized using **Ru3** catalyst>



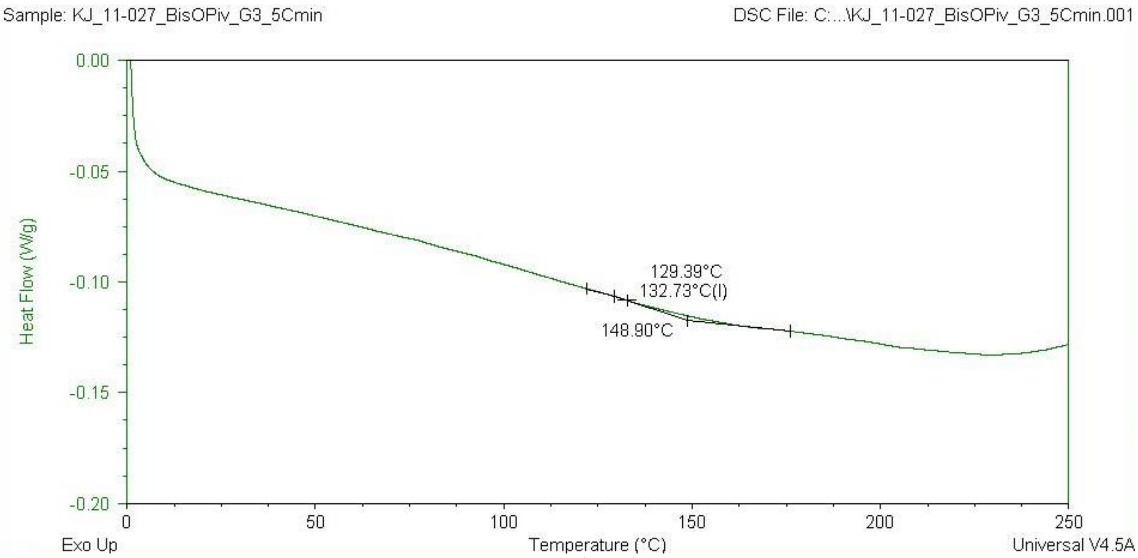

<Figure S28. TGA curves of Poly(M11) synthesized using Ru1 catalyst>



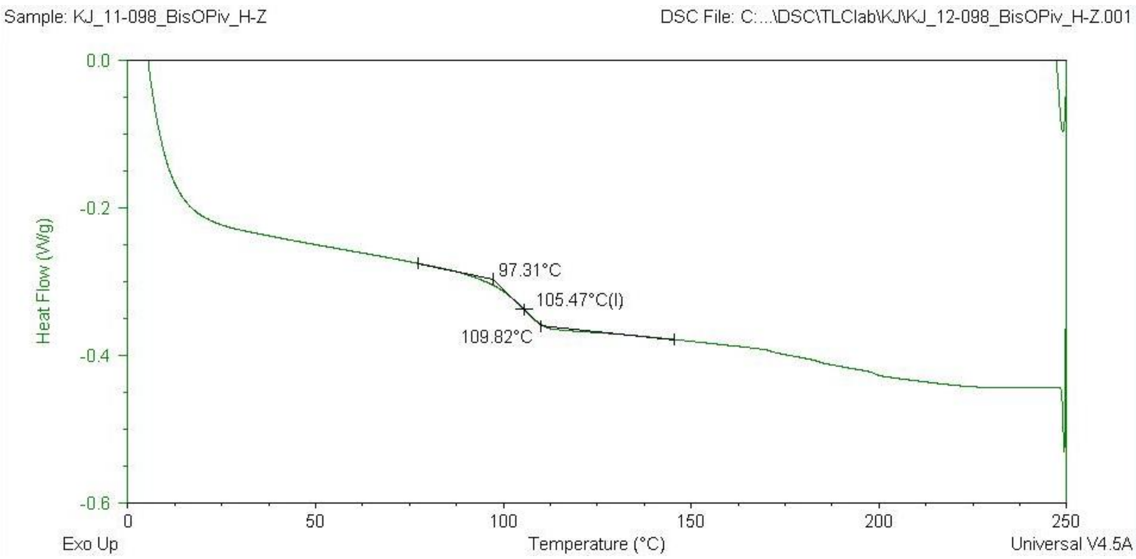

<Figure S29. TGA curves of Poly(M11) synthesized using Ru3 catalyst>



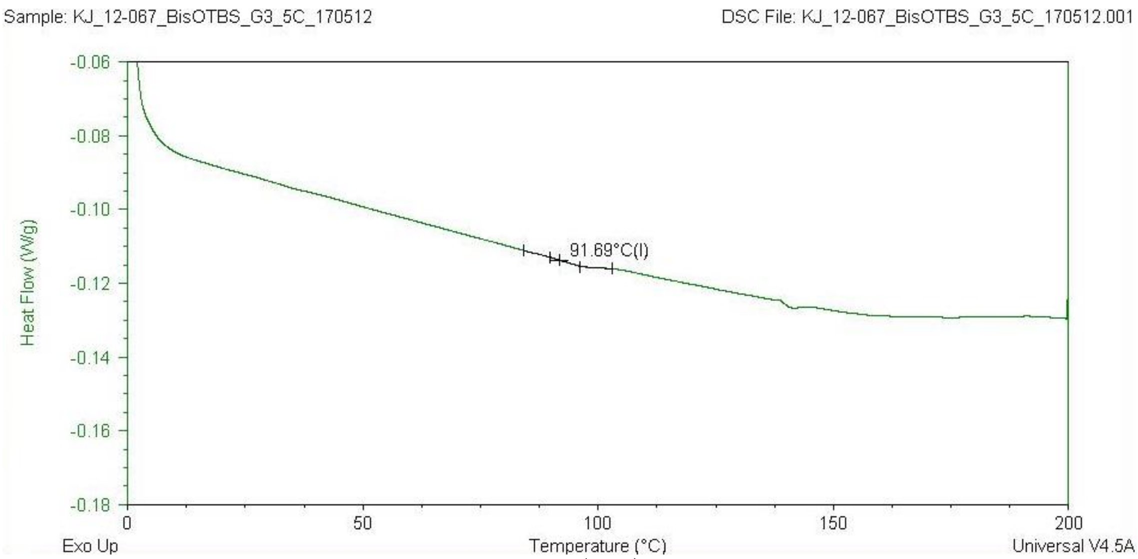
<**Figure S30.** DSC thermogram of Poly(**M3**) synthesized using **Ru3** catalyst>



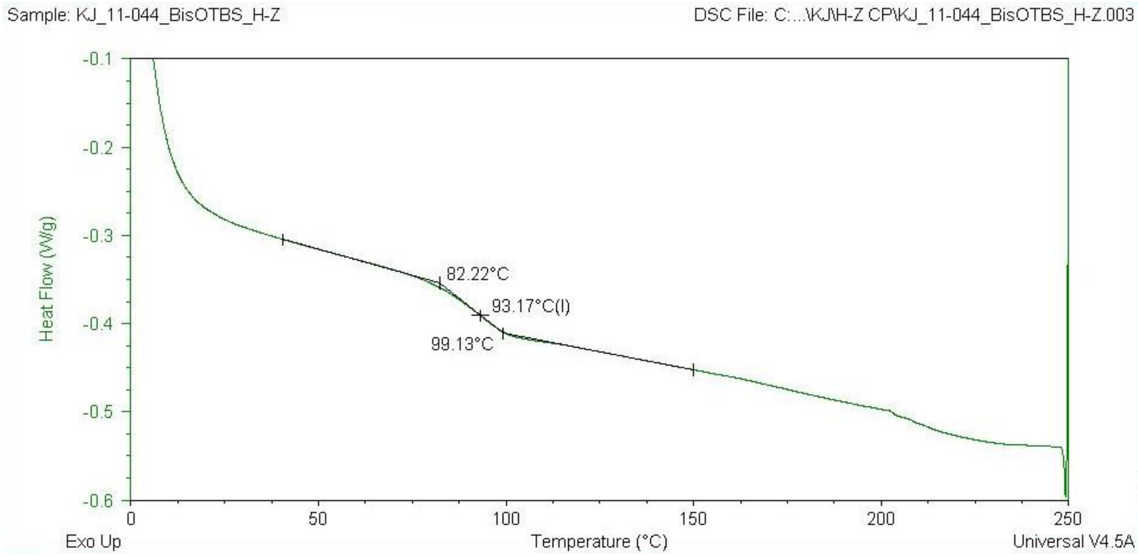
<**Figure S31.** DSC thermogram of Poly(**M5**) synthesized using **Ru1** catalyst>



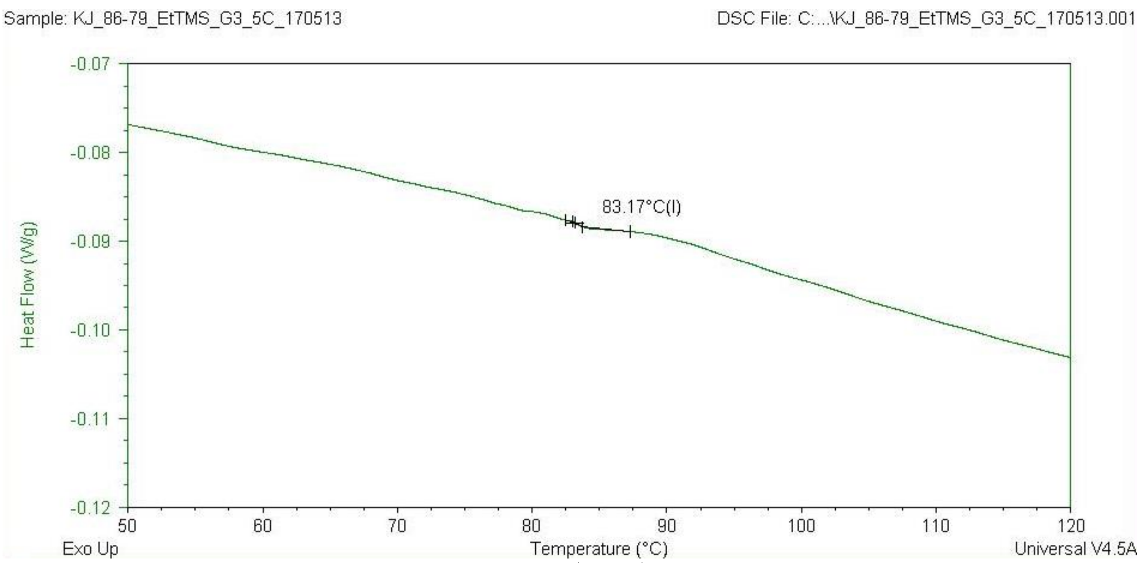
<**Figure S32.** DSC thermogram of Poly(**M5**) synthesized using **Ru3** catalyst>



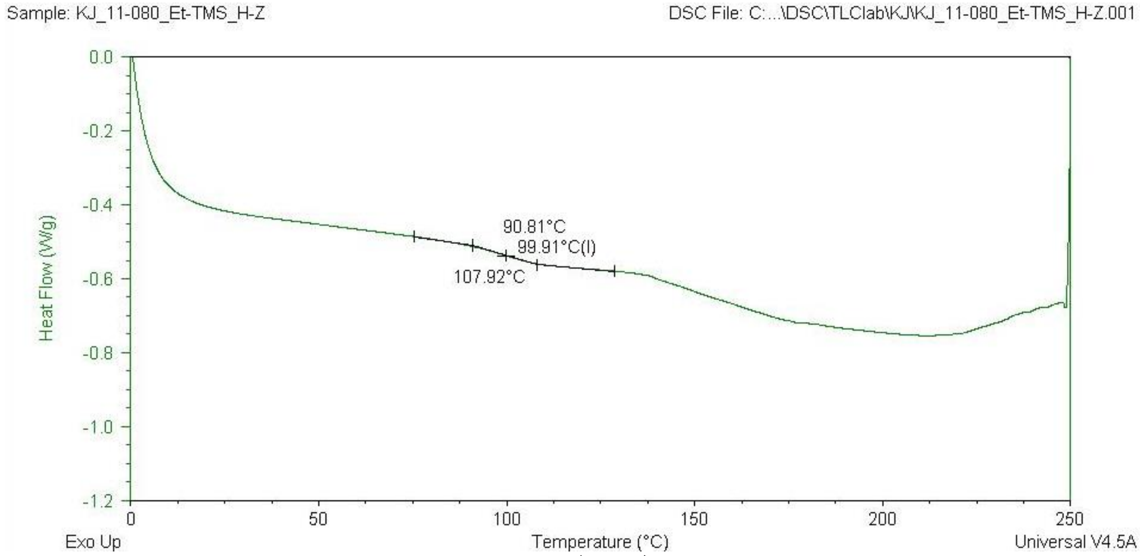
<**Figure S33.** DSC thermogram of Poly(**M7**) synthesized using **Ru1** catalyst>



<**Figure S34.** DSC thermogram of Poly(**M7**) synthesized using **Ru3** catalyst>



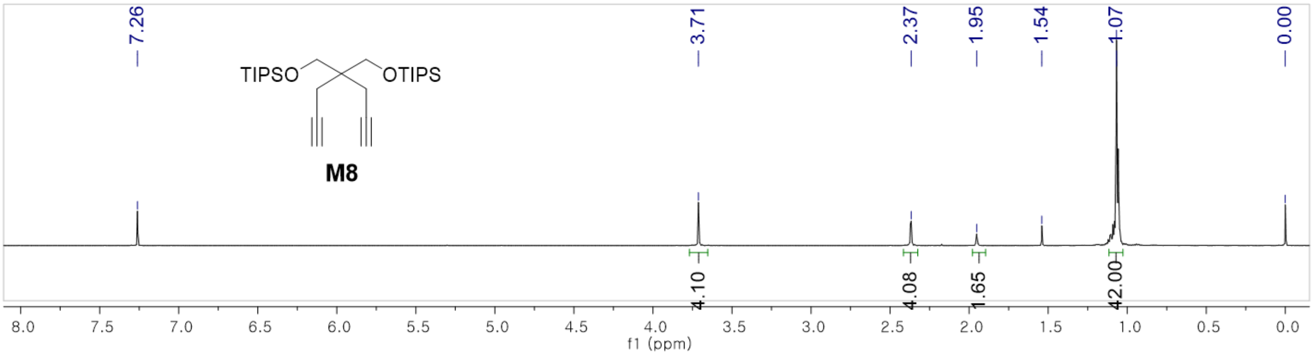
<**Figure S35.** DSC thermogram of Poly(**M11**) synthesized using **Ru1** catalyst>



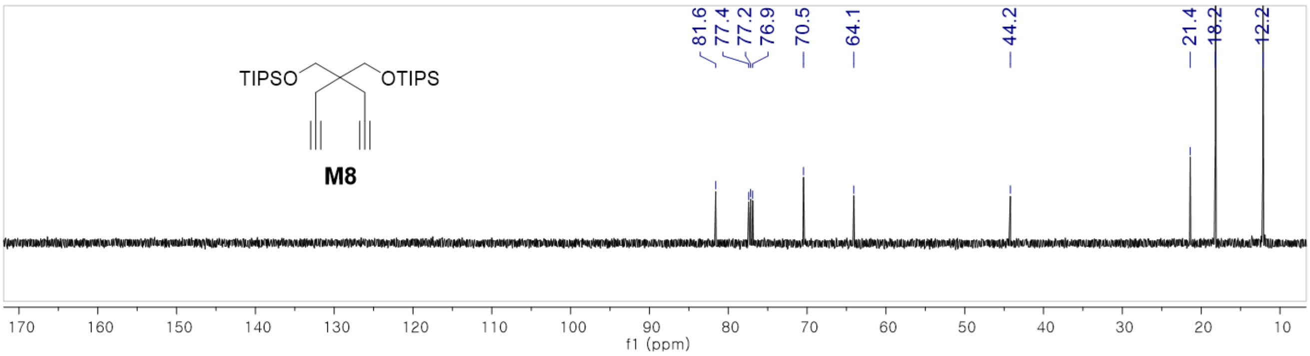

<**Figure S36.** DSC thermogram of Poly(**M11**) synthesized using **Ru3** catalyst>

## 12. $^1H$ and $^{13}C$ NMR spectra of the monomers

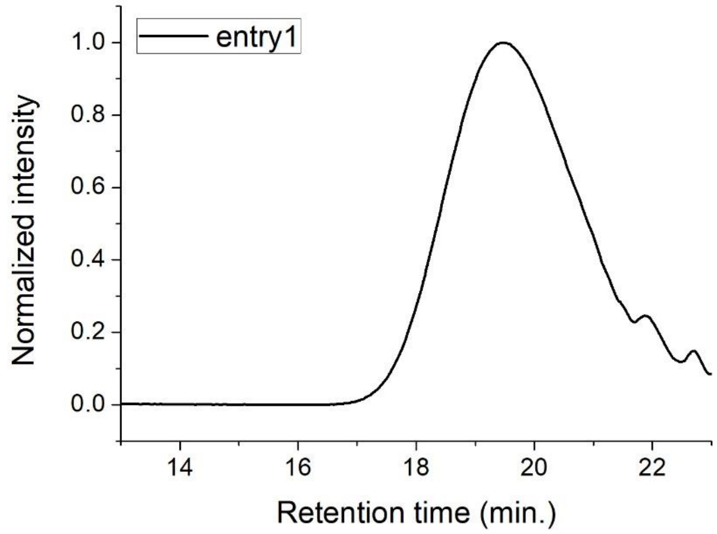
**M8** ($^1H$, 400 MHz, $CDCl_3$)

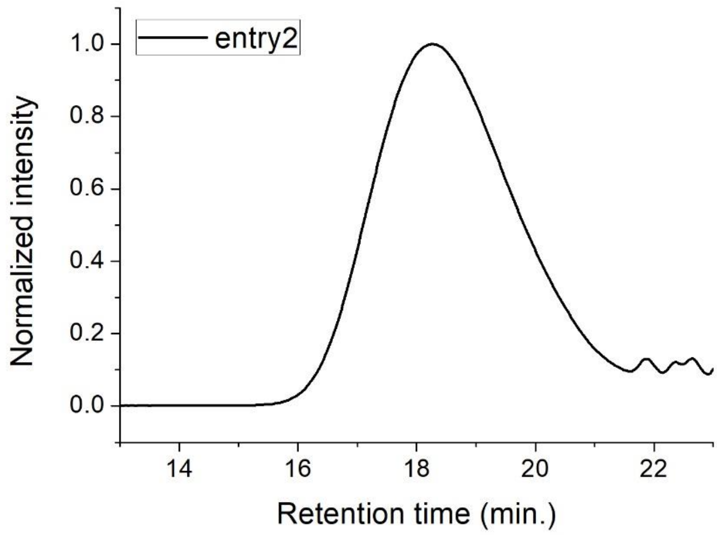


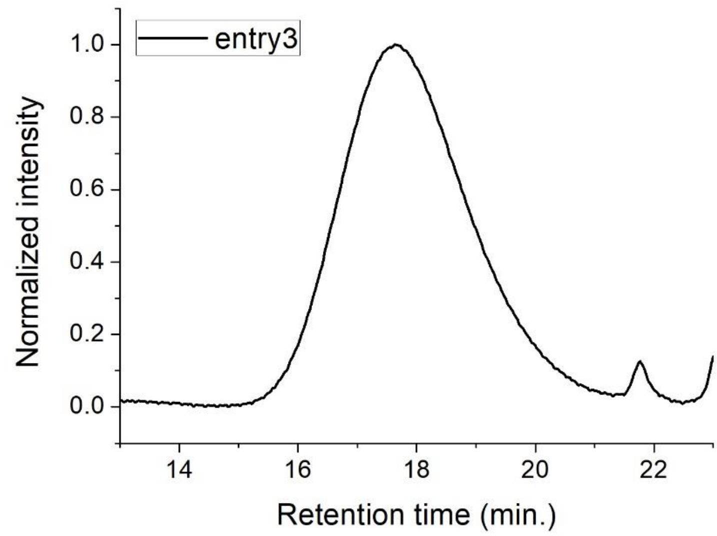

**M8** ($^{13}C$, 100 MHz, $CDCl_3$)

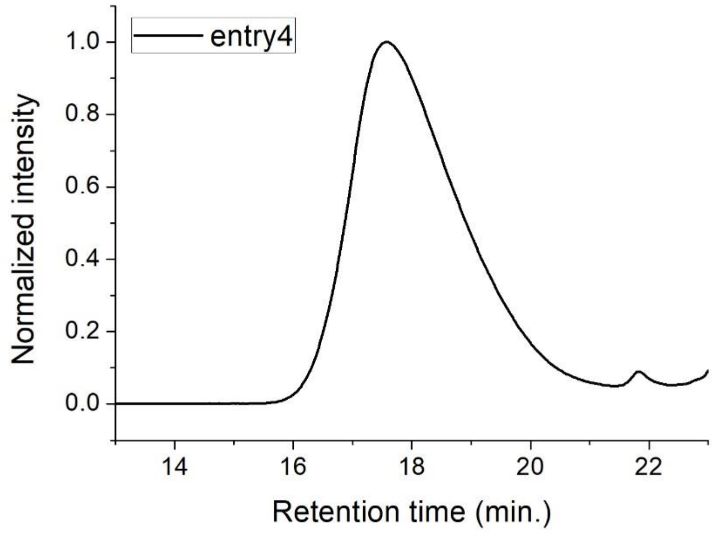


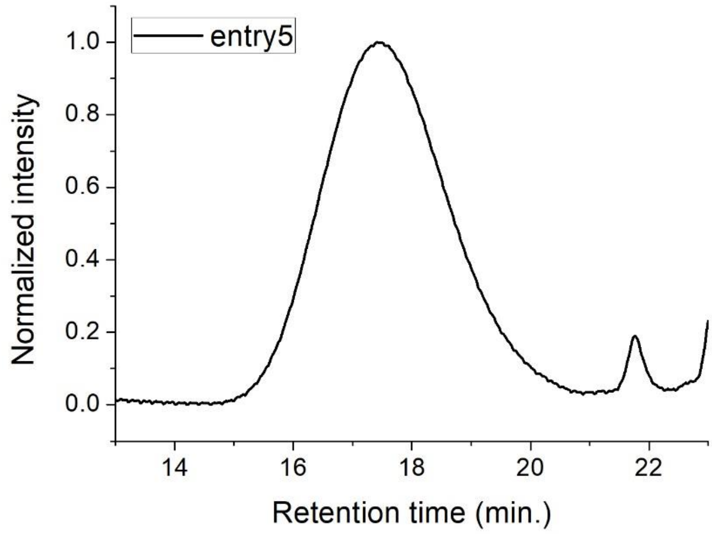
## 13. SEC traces of the polymers in Table 1

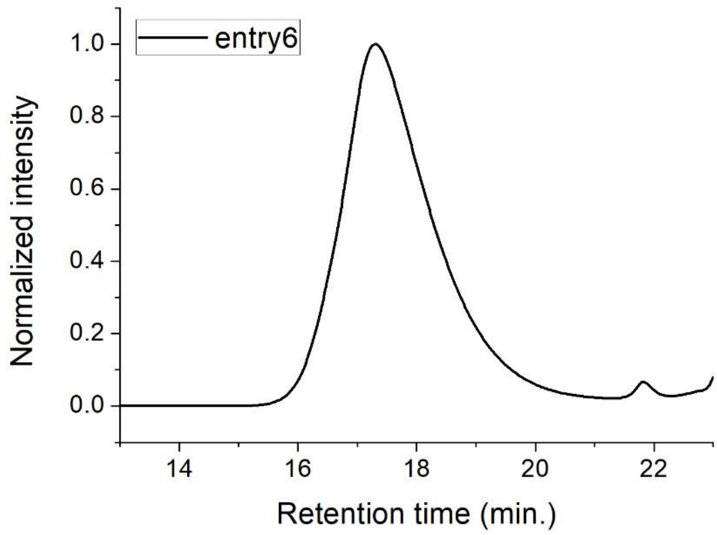


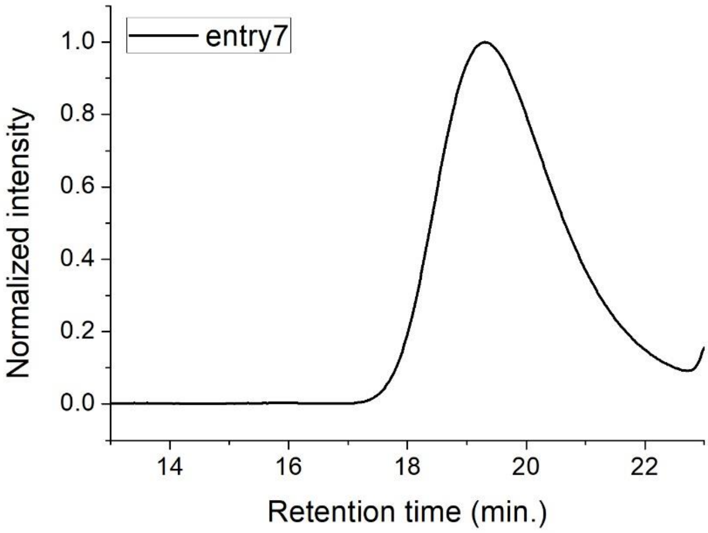



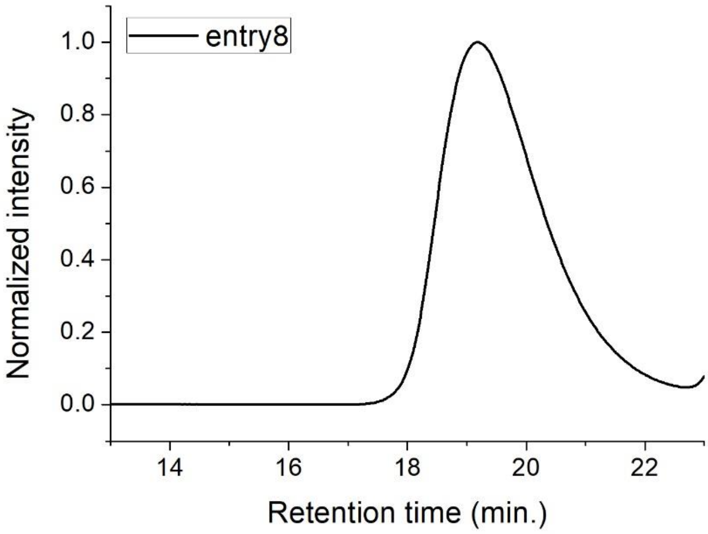



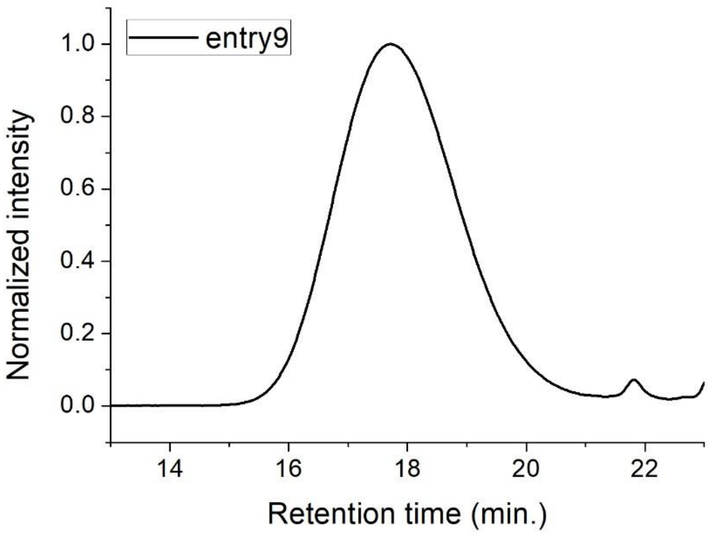

entry4
Normalized intensity
Retention time (min.)
1.0
0.8
0.6
0.4
0.2
0.0
14
16
18
20
22

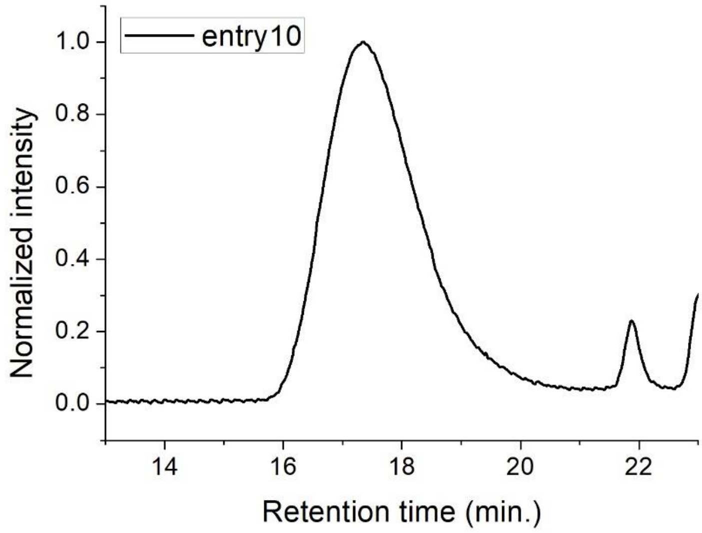

entry5
Normalized intensity
Retention time (min.)
1.0
0.8
0.6
0.4
0.2
0.0
14
16
18
20
22


entry6
Normalized intensity
Retention time (min.)
1.0
0.8
0.6
0.4
0.2
0.0
14
16
18
20
22

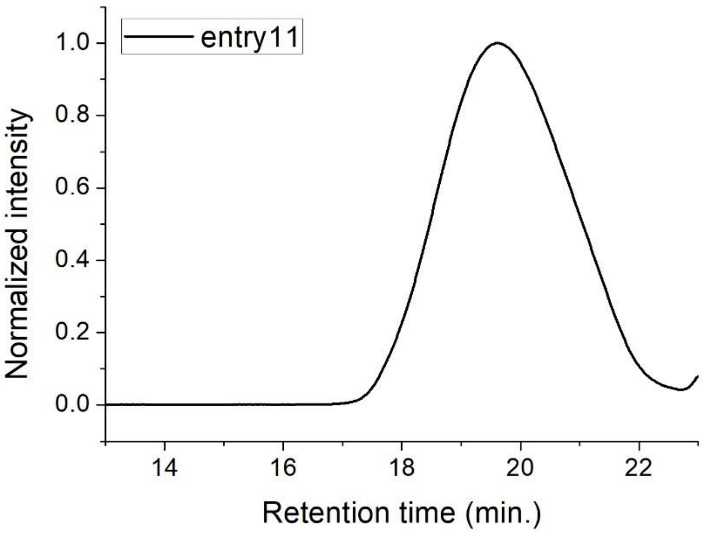

entry7
Normalized intensity
Retention time (min.)


entry8
Normalized intensity
Retention time (min.)

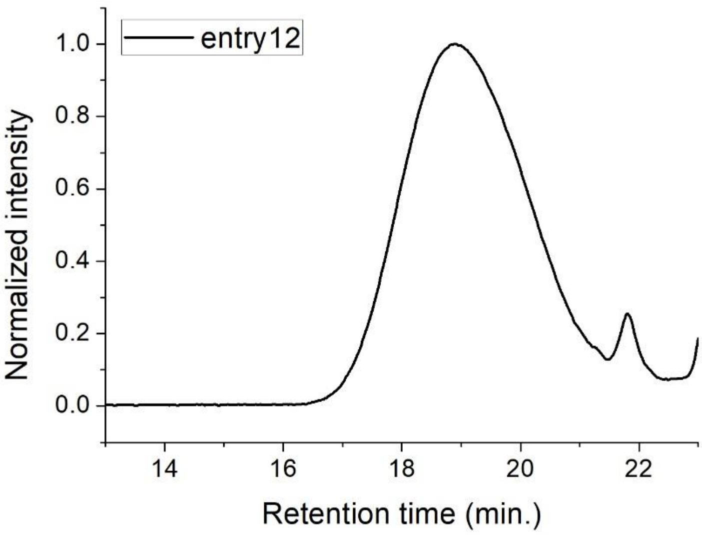

entry9
Normalized intensity
Retention time (min.)



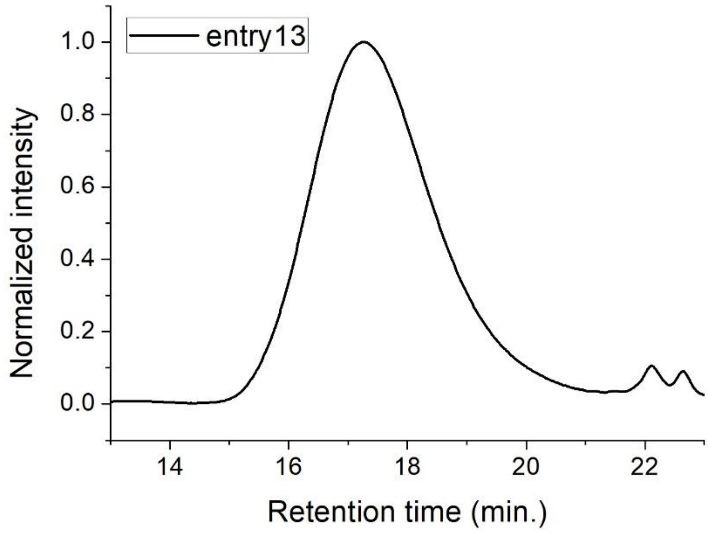
entry10
Normalized intensity
Retention time (min.)

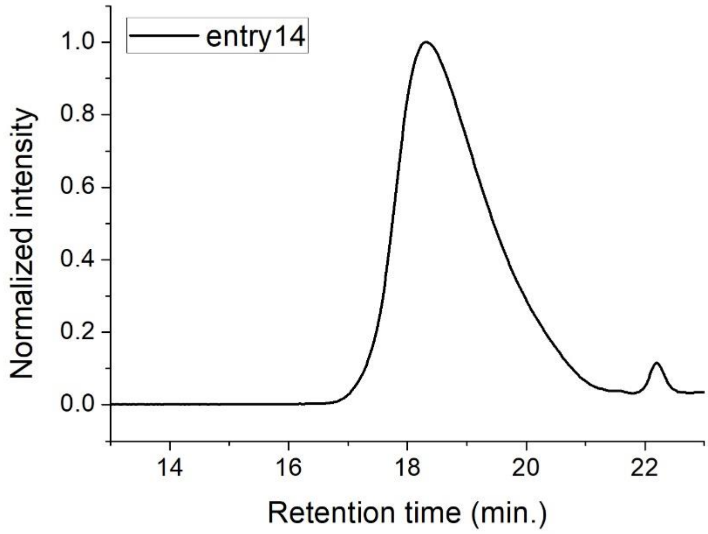



entry11
Normalized intensity
Retention time (min.)

entry12
Normalized intensity
Retention time (min.)


entry13
Normalized intensity
Retention time (min.)
1.0
0.8
0.6
0.4
0.2
0.0
14
16
18
20
22


entry14
Normalized intensity
Retention time (min.)
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0.8
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0.2
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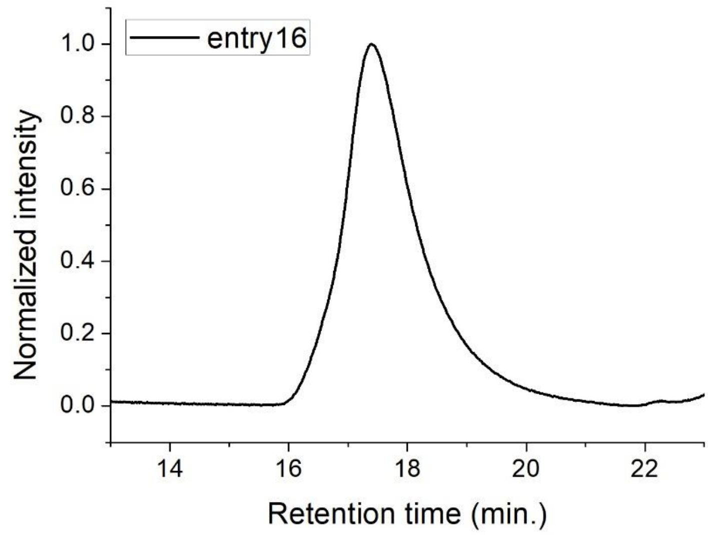
14
16
18
20
22


entry16
Normalized intensity
Retention time (min.)
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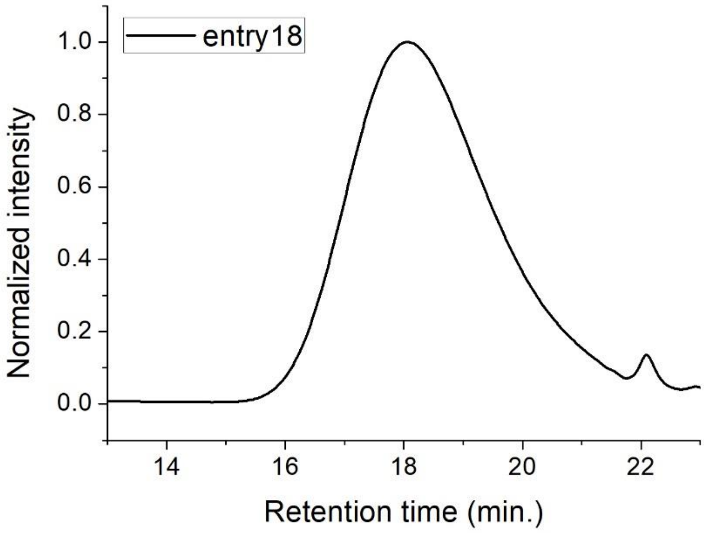
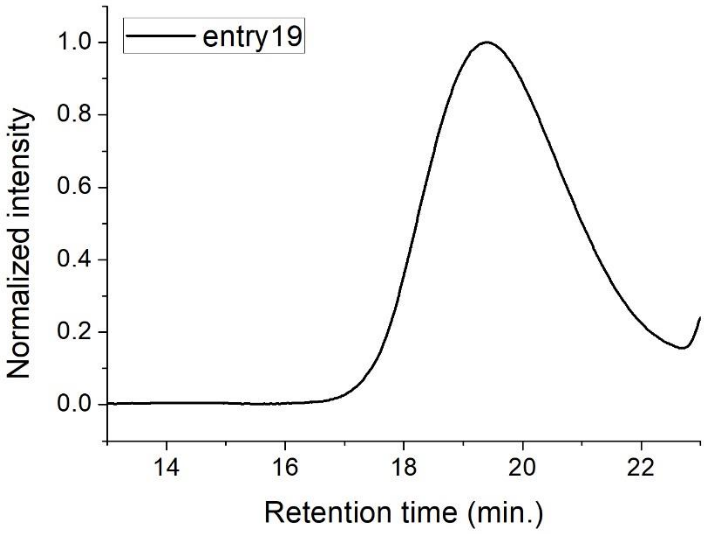
0.6
0.4
0.2
0.0
14
16
18
20
22


entry18
Normalized intensity
1.0
0.8
0.6
0.4
0.2
0.0
14
16
18
20
22
Retention time (min.)


entry19
Normalized intensity
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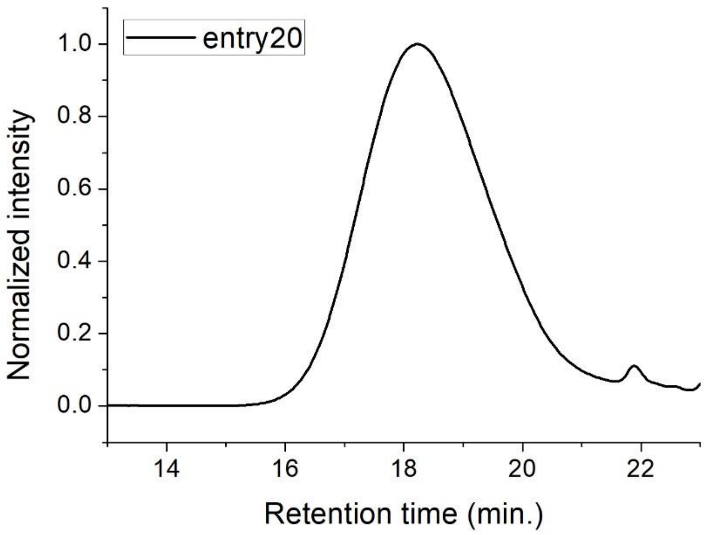
0.6
0.4
0.2
0.0
14
16
18
20
22
Retention time (min.)


entry20
Normalized intensity
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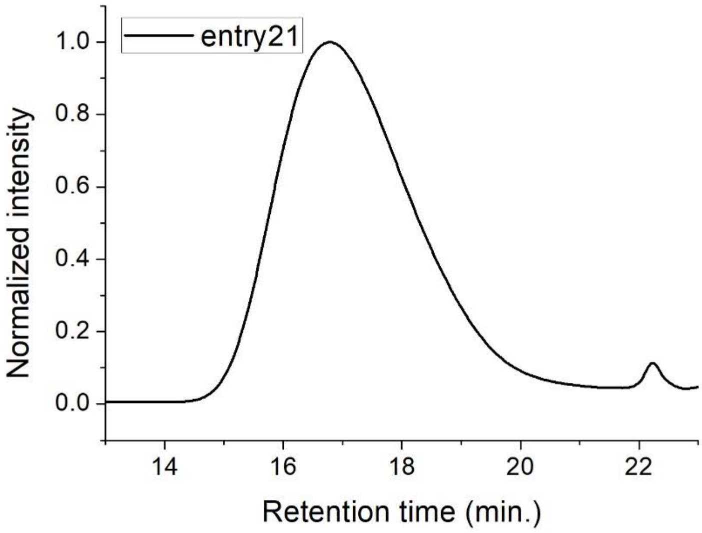
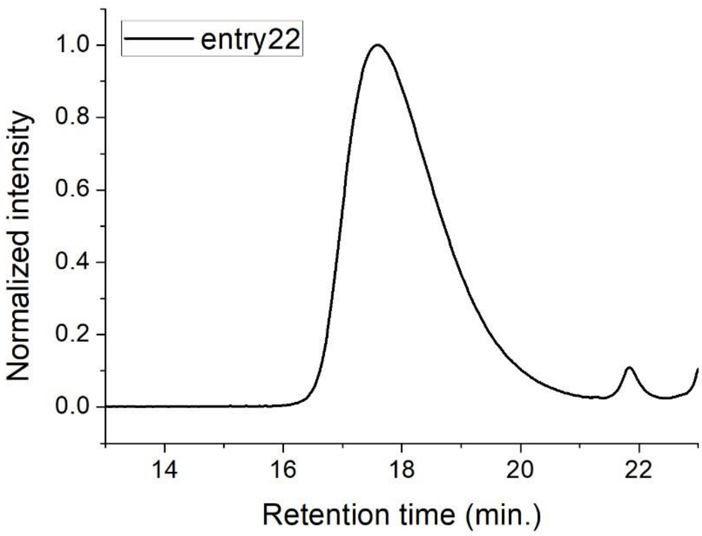
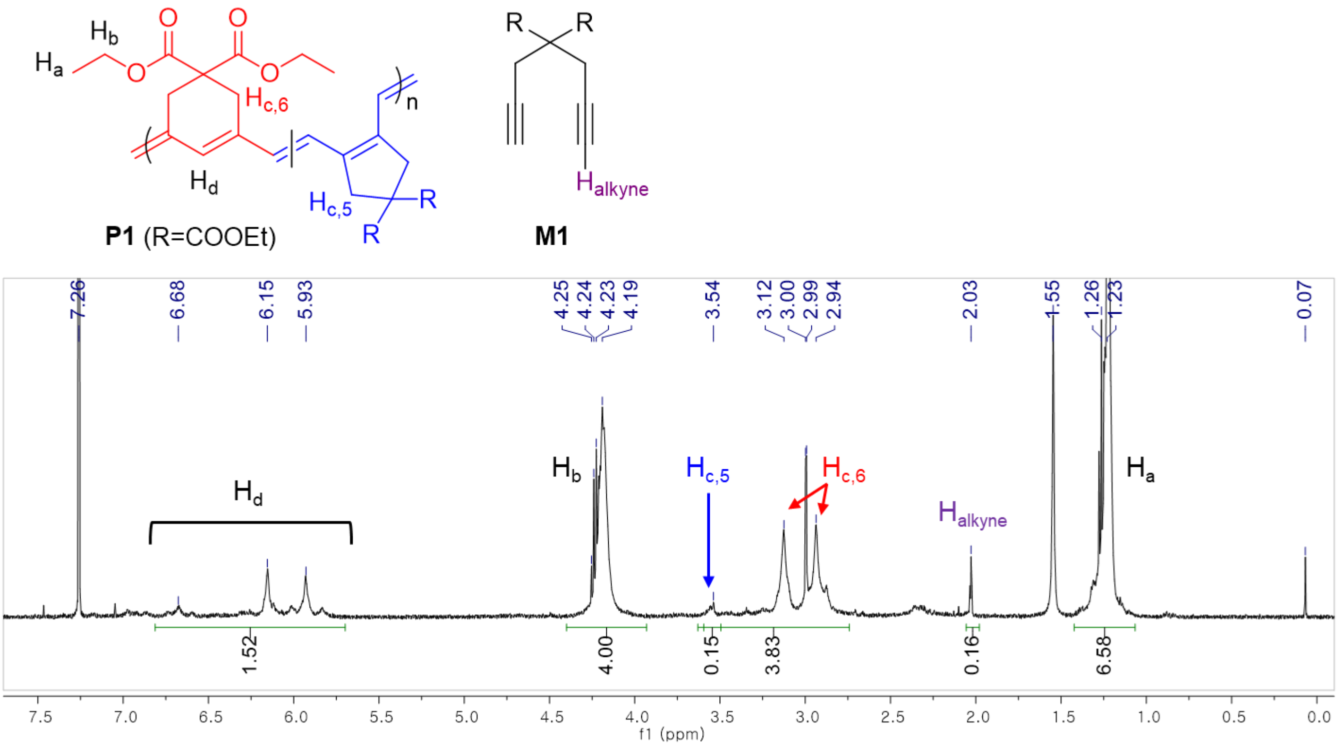
0.6
0.4
0.2
0.0
14
16
18
20
22
Retention time (min.)


entry21
Normalized intensity
Retention time (min.)
0.0
0.2
0.4
0.6
0.8
1.0
14
16
18
20
22


entry22
Normalized intensity
Retention time (min.)
0.0
0.2
0.4
0.6
0.8
1.0
14
16
18
20
22

## 14. Calculation of the regioselectivity for P1 using $^{1}$H NMR




<**Figure S37.** $^{1}$H NMR spectrum of the crude mixture of entry 2 in Table 1>

$$\text{Monomer conversion} = 1 - \frac{H_{alkyne}}{2.0}$$

$$\text{Composition of five-membered ring} = \frac{2 * H_{c,5}/H_{\text{originated from propargylic}}}{\text{Monomer conversion}}$$

e.g. (entry 2 in Table 1)

$$\text{Composition of five-membered ring} = \frac{2*0.15/3.83}{0.91} = 0.086 \quad (\therefore \text{6-ring:5-ring=11.6:1})$$

## 15. References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